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SOME FUNDAMENTAL MEASUREMENTS ON
FISCHER TROPSCH CATALYSTS

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SOME FUNDAMENTAL MEASUREMENTS
ON FISCHER TROPSCH CATALYSTS

Measurements of surface area of a $\text{CO} : \text{ThO}_2 : \text{MgO} :$
bentonite catalyst and the rates of decomposition of
some oxygenated compounds over a $\text{CO} : \text{ThO}_2 : \text{MgO} :$
filtercel catalyst.

Submitted in Partial Fulfilment
of the

Requirements for the Degree of

MASTER OF SCIENCE

by

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under the direction of

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PART I

INTRODUCTION

The synthesis of hydrocarbons in the gasoline range was first investigated by Fischer and Tropsch in 1925. Synthesis gas, consisting of carbon monoxide and hydrogen in the ratio of 1:2, when passed over a cobalt, nickel or iron catalyst formed hydrocarbons with a small amount of oxygenated compounds. The optimum conditions found were a temperature of 200°C. and a moderate pressure between one atmosphere and seven atmospheres. In 1934 Ruhrchemie undertook industrial development of the process and by 1936 the first industrial plant was in operation. By 1940, one million tons per year of synthetic hydrocarbons were being produced. Plants were also built in France, Japan, Manchukuo and planned for other areas. Today commercial plants using natural gas and oxygen as raw materials are planned for gas fields in the United States.

The original purpose of the Fischer Tropsch process was to produce liquid hydrocarbons for internal combustion engines. These are still the most important products, but the by-products are important for the production of aliphatic compounds for chemical industry.

However, no fundamental knowledge of the requirements for a good catalyst was available and a method of trial and error had been used exclusively in the early work of Fischer and his co-workers.

Not only the composition of the catalyst and the supporting medium but also the conditions of pressure, rate of gas flow, and indeed the whole synthesis procedure as first evolved was based on

purely empirical data. On this basis the German industries designed their practical, though probably uneconomic plants. However, before English and American capital could be interested in similar plants, more knowledge of the process was necessary. Cost and efficiency factors which the Germans could afford to ignore in their great need for hydrocarbon fuel could not be ignored by companies which must compete both with crude oil and with other possible synthesis processes.

With this incentive in mind many approaches to the problem have been pursued in recent years. These studies have not only been directed towards finding new catalysts but also towards obtaining a better understanding of the catalysts already known.

The work carried out by Boomer and others at the University of Alberta has primarily been aimed at determining the activity of new catalysts and the conditions under which they would operate most satisfactorily.

In the investigation reported here a measurement of the surface area of a catalyst with a bentonite carrier was made. This property was compared with that of a catalyst with a kieselguhr carrier. The catalytic activity was compared with that of other catalysts containing different carriers.

The rates of decomposition of various oxygenated compounds over a cobalt catalyst have been determined together with their activation energies. It was hoped that the information might aid in determining the mechanism of the synthesis reaction.

THE THEORY OF ADSORPTION

Adsorption⁽¹⁾ is an increase in the concentration of a substance on a surface or at the boundary of two phases. The type of adsorption occurring most frequently is positive in character and corresponds to an increase in the concentration at the boundary. When the adsorbed substance does not remain at the boundary but is carried into the adsorbent, the phenomena is known as absorption or sorption, corresponding to a solution in the interior of the adsorbent. The term sorption is often applied to gases adsorbed either on carbon or on metals. Absorption on or solution in metals corresponds to an occlusion.

Adsorption negative in character is rare. Negative adsorption takes place when the solvent for the substance to be adsorbed is to a great extent adsorbed itself. Typical examples of this occur in the use of gels.

The solid that takes up the gas or vapor⁽²⁾ is called the adsorbent. The gas or vapor attached to the surface of the solid is called the adsorbate. If the gas enters the inside of a solid, two things may happen. Either the gas merely dissolves in it, forming a solid solution, or it reacts with the solid and forms a compound. If the gas remains attached to the surface of the solid, again two things may happen. First, there may be a weak interaction between solid and gas, similar to condensation, or, second, there may be a strong interaction, similar to chemical reactions. The former is called physical adsorption or Van der Waal's adsorption, and the latter is called chemical adsorption or chemisorption. Van der Waal's adsorption implies that the same forces that are active in condensation,

that is, the Van der Waal's forces, are also active in physical adsorption.

When a gas or vapor is admitted to a thoroughly evacuated adsorbent its molecules distribute themselves between the gas phase and the adsorbed phase. The disappearance of the molecules from the gas phase occurs with great rapidity in some cases, in others at a measurable rate. After a while the process stops and a state of stable equilibrium is reached. The amount of gas adsorbed per gram of adsorbent at equilibrium is a function of the temperature, the pressure and the nature of the adsorbent and the adsorbate.

For a given gas and unit weight of a given adsorbent the amount of gas adsorbed at equilibrium is a function of the final pressure and temperature only.

$$(1) \quad a = f(p, T)$$

where a = the amount adsorbed per gram of adsorbent,
 p = the equilibrium pressure,
 T = the absolute temperature

When the pressure of the gas is varied and the temperature is kept constant, the plot of the amount adsorbed against the pressure is called the adsorption isotherm, and the equation is:

$$(2) \quad a = f(p)$$

$$T = \text{constant}$$

When the temperature is varied and the pressure kept constant one obtains the adsorption isobar.

$$(3) \quad a = f(T)$$

$p = \text{constant}$, for the adsorption isostere, that is, the variation of the equilibrium pressure with respect to the temperature for a definite amount of gas adsorbed.

$$(4) \quad p = f(T)$$

$$a = \text{constant}$$

The Adsorption Isotherm

At constant temperature the adsorption of a gas or vapor increases with increasing pressure. In Fig. 1 adsorption isotherms of ammonia on charcoal are shown.

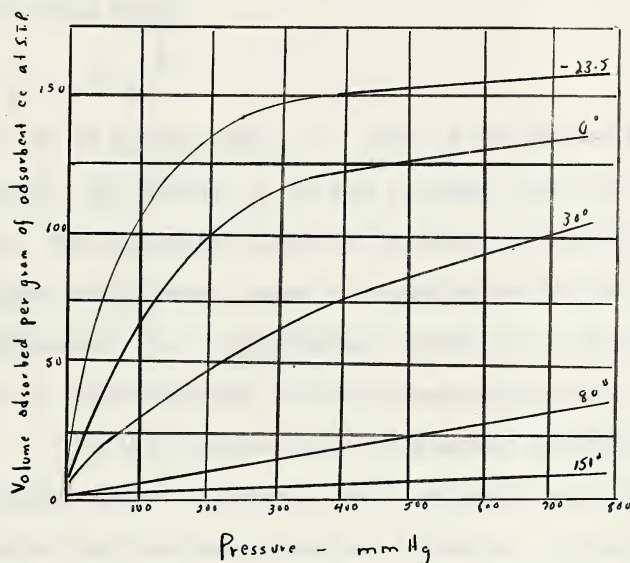


Fig. 1

The above curves represent pure physical adsorption, even at highest temperatures.

Since the adsorption process is always exothermic, the amount adsorbed at equilibrium must always decrease with increasing temperature according to the principle of Le Chatelier. Fig. 1 shows that this is actually the case: the lower the temperature the greater the adsorption. At small adsorptions the volume increases

linearly with pressure. The 151.5°C . isotherm obeys Henry's Law:

$$v = kp$$

where v is the volume adsorbed,
 p is the pressure

At somewhat higher adsorptions for equal increments of p the increments of v become smaller and smaller. The volume adsorbed becomes proportional to a power of the gas pressure smaller than unity,

$$v = k^{\frac{1}{n}} p^{\frac{1}{n}}$$

where n is greater than 1. This is the Freundlich isotherm equation. The factor n is not constant over any large pressure range. The Freundlich equation expresses satisfactorily the adsorption of a gas over a small range of pressure but has not any fundamental significance. It is particularly useful as an interpolation equation where it can be made to fit the experimental data.

In 1915 two entirely independent theories were proposed by Polanyi and by Langmuir. Their approach was different. Langmuir believed that the adsorption was a chemical process and that the adsorbed layer was unimolecular. Polanyi believed the adsorption was a physical process and that the adsorbed phase was many layers thick. Both treatments were successful in many instances and both have their limitations. The Polanyi theory applies to Van der Waal's adsorption only, the Langmuir theory applies within limits to both chemical and physical adsorption.

Langmuir made three assumptions as the basis of his derivative:

(1) That the attraction between the molecules is less than the attraction between a molecule and the adsorbing surface.

(2) That the probability of evaporation of a molecule from the surface is the same whether the neighboring positions are filled or not.

(3) That molecules striking adsorbed molecules are elastically reflected and only those striking the bare surface have a chance to be adsorbed.

Therefore the Langmuir⁽²⁰⁾ adsorption isotherm may be written as:

$$y = \frac{a P}{1 + b P}$$

where y = amount of gas adsorbed per unit area or per unit mass of adsorbent.

P = pressure

$b = \frac{k_1}{k_2}$ constants of proportionality

a = constant

'a' and 'b' are evaluated from experimental data.

Polanyi assumed that the adsorbed gas acts as a compressed film on the surface and obeys the same equation of state as in the gas phase, he derived equations for expressing θ , the potential as a function of ϕ , the volume adsorbed. The θ, ϕ curve is independent of temperature. It can be plotted from one experimentally determined isotherm and other isotherms plotted from it. Although the physical concept of adsorption upon which this theory is based has been discarded, it does correctly express the temperature dependence of adsorption for the system to which it is applicable.

The capillary condensation theory attributes adsorption to condensation of the gas in the capillaries of the adsorbent. It has long been known that a liquid wetting the wall of a capillary has a lower vapor pressure in the capillary than in the normal bulk phase.

This behavior was extrapolated to capillaries of molecular dimensions. Zsigmondy assumed that in such very small capillaries condensation can take place at pressures considerably lower than the normal vapor pressure. The capillaries at the smallest radii fill at the lowest pressure. As the pressure is increased, always larger capillaries fill, until finally at the saturation pressure all the pores of the adsorbent fill with liquid.

Another theory based on the assumption that physical adsorption is more than one molecular layer thick is the polarization theory proposed by de Boer and Zwikker in 1929. It explains the adsorption of non-polar molecules on ionic adsorbents by assuming that the uppermost layer of the adsorbent induces dipoles in the first layer of adsorbed molecules which in turn induce dipoles in the next layer and so on until several layers are built up.

Brunauer, Emmet and Teller⁽³⁾ in 1938 proposed that the same forces that produce condensation are also chiefly responsible for the binding energy of multimolecular adsorption, which shall be called the multimolecular adsorption.

According to both the polarization theory and the multimolecular adsorption theory the forces involved in adsorption are short range forces, that is, only the first adsorbed layer is attracted strongly by the surface. The second layer is adsorbed essentially, not by the surface, but by the first adsorbed layer and the adsorption propagates from layer to layer. The two theories differ from each other with respect to the type of forces that are assumed to produce the adsorption. According to the polarization theory adsorption is due to induced dipoles. According to the multimolecular adsorption theory it is due to the totality of forces

usually designated as Van der Waal's forces.

The polarization equation

$$l_n \frac{P_n}{K_3 P_0} = K_2 K_1^n$$

where n = no. of layers

Brunauer, Emmet and Teller in 1938 proposed a theory of multimolecular adsorption which is now generally accepted as a good approximation in most cases.

The following isotherm equation was derived for multimolecular adsorption on a free surface. (5)

$$\frac{P}{v (P_0 - P)} = \frac{1}{v_m C} + \frac{C - 1}{v_m C} \cdot \frac{P}{P_0} \quad (A)$$

where v is the volume adsorbed at pressure P and absolute temperature T
 P_0 is the vapor pressure of the gas at temperature T
 v_n is the volume of gas adsorbed when the entire adsorbent surface is covered with a unimolecular layer
 C is a constant characteristic of the system

If one plots the function of $\frac{P}{v (P_0 - P)}$ against $\frac{P}{P_0}$ one

obtains a straight line whose slope and intercept give the values of v_n and C . The surface area of the adsorbent can be calculated from a knowledge of the size of the adsorbed molecule.

If the adsorption takes place in a limited space, so that even at saturation pressure only a limited number of layers can be adsorbed on the adsorbent, one obtains the expression:

$$v = \frac{v_m C x}{1 - x} \cdot \frac{1 - (n + 1) x^n + n x^{n+1}}{1 + (C - 1) x - C x^{n+1}} \quad (B)$$

where $x = \frac{P}{P_0}$, v_m and C have the same meaning as before,

and n is the maximum number of layers of adsorbed gas that can build up on the walls of the capillaries, supposedly of plane parallel sides.

Equation (B) reduces to (A) when $n = \infty$; and in the other extreme case when only one adsorbed layer can form on the surface, that is, when $n = 1$, it reduces to the Langmuir type equation:

$$\frac{P}{v} = \frac{P_0}{C v_m} + \frac{P}{v_m} \quad (C)$$

A search in the literature on the Van der Waal's adsorption of gases reveals that there exist five different types of isotherms.

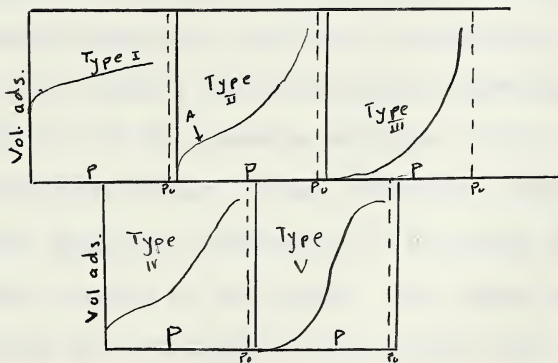


Fig. 2

Type I is the well known Langmuir adsorption isotherm.

Equation (C) describes a Type I isotherm, and equations (A) and (B) describe Type II isotherms where $C \gg 1$ or E_1 , (heat of adsorption of the gas in the first layer), is greater than E_L , (heat of liquefaction of the gas); in other words, when the

attractive forces between adsorbed gas and adsorbent are greater than the attractive forces between the molecules of the gas in the liquefied state. It should be noted, however, that when the forces between adsorbent and adsorbate are small, that is, when $E_1 < E_L$ -- then equations (A) and (B) describe Type III isotherm. The point 'A' on the curve of Type II isotherm indicates the completion of the first layer of molecules.

Types IV and V suggest that the complete, or almost complete, filling of the pores and capillaries of the adsorbent occurs at a pressure lower than the vapor pressure of the gas. This lowering of the vapor pressure indicates that as the pressure of the gas is increased some additional forces appear that make the heat of adsorption or energy of binding in some higher layer to be greater than E_L , the heat of liquefaction of the gas. This must be necessarily so, since the last adsorbed layer in a capillary is attracted on both sides, and therefore its heat of evaporation must be greater than that of any other layer, with the possible exception of the first layer where the adsorptive forces are very different. Types IV and V show evidences that capillary condensation is occurring at pressures less than the vapor pressure of the liquid. The simple expression of B.E.T. equation does not apply to these rather rare cases. The equation derived by Brunauer, Emmet and Teller for these cases is much more complex and involved. Three further assumptions to those already used are:

1. That the capillaries are of uniform size.
2. That the walls of the capillaries are plane parallel surfaces.
3. That the capillaries are open on the sides,⁽²¹⁾

As pointed out by Brunauer⁽²⁾ this theory is open to criticism, in that it has several limitations. At low pressures it reduces to the Langmuir equation, consequently all the criticism that has been levelled against the Langmuir theory can be directed equally well against the multimolecular adsorption theory in the low pressure region of the adsorption isotherm. The most active parts of the surfaces of most adsorbents are strongly heterogeneous, with strongly varying heats of adsorption, therefore the Langmuir equation is not obeyed. For most adsorbents the theory breaks down in the region from zero pressure to $\frac{P}{P_0} = 0.05$, and for some adsorbents as high as 0.10.

The multimolecular adsorption theory is at its best in the middle adsorption region, that is, the region preceeding and following the building up of a unimolecular layer. Since most adsorbents have capillaries that are at least several molecular diameters wide, the difficulties due to capillary condensation do not yet begin to appear in this region. Thus the two-constant equation (A) is obeyed very closely for many adsorbents to at least $\frac{P}{P_0} = 0.35$ and sometimes to .50.

THE MEASUREMENT OF SURFACE AREAS

Porous materials⁽¹⁶⁾ are usually considered to have 'inner' as well as 'outer' surfaces. The 'inner' surface comprises the surface of the cracks, crevices and capillaries that extend into the individual particles. The 'outer' surface is, roughly speaking, the portion of a porous material subjected to direct and free bombardment by the molecules of the enveloping gas. The 'total' surface area refers to the sum of the areas of the 'inner' and 'outer' surfaces.

It is at once evident that different values for the area of the total surface of a porous material are likely to be obtained depending upon the particular method used for making the measurements. The present discussion will, therefore, be restricted to those methods of measuring surface areas that depend upon measuring the volume of gas adsorbed by the solid catalyst. Such methods in general have the advantage of being applicable to all types of porous or finely divided catalysts, including those whose nature and surface might be altered by suspension in any of the liquid media that are common to a number of methods for measuring surface areas.

If the volume of some gas such as nitrogen or argon required to form a physically adsorbed monolayer over the entire 'inner' and 'outer' surface of a catalyst can be determined, the total area can be calculated by multiplying the cross sectional area of each adsorbed molecule by the number of molecules in the monolayer.

It is evident that the reliability of the method will depend largely upon the accuracy with which one can choose the point on the isotherm corresponding to a monolayer. A multiplication of the

number of molecules⁽¹²⁾ required to form the single layer by the average area occupied by each adsorbed molecule yields a numerical value for the absolute area of a given weight of absorbent. The absolute surface area values obtained obviously depend upon the accuracy with which the point corresponding to a monomolecular adsorbed layer can be picked. Originally this point (designated as 'A' in Isotherm II, Fig. 2), was selected empirically as the lower pressure extremity of the long linear portion of the experimental adsorption isotherm.

Therefore if we write the B.E.T. equation in the form,

$$\frac{P}{v} = \frac{1}{(v_m b)} + (P/v_m)$$

it is obvious that a plot of P/v against P will be a straight line of slope $\frac{1}{v_m}$. The surface area can be calculated if the size of the adsorbed molecule is known. The above equation is, as previously noted, the Langmuir isotherm.

Certain precautions are necessary in the choice of experimental conditions in order that v_m should represent a monomolecular layer over the whole surface and not just the more active parts. The adsorption should be measured at pressures close to the vapor pressure at any particular temperature, which means in most cases working at temperatures only slightly higher than the boiling point at atmospheric pressure.

When the isotherm is of Type II, the B.E.T. equation applies. The best range of application is of a relative pressure of .1 to .4 and at a temperature only slightly above the boiling point.

If $\frac{P}{v (P_0 - P)}$ is plotted against $\frac{P}{P_0}$ both v_m and

C can be evaluated.

In the majority of cases it is satisfactory to take only one or two measurements of adsorption corresponding to a relative pressure of about 0.4. When C is large the slope of the line joining this one point to the origin in the plot of $\frac{P}{P_0}$ versus

$\frac{P}{v (P_0 - P)}$ is $\frac{1}{v_m}$ within the limits of experimental error,

since $(C-1)$ and C are approximately equal and the intercept $\frac{1}{v_m C}$ will be negligibly small.

In this investigation all surface areas were measured using nitrogen as the adsorbed gas at a temperature of 83°K . At this temperature the vapor pressure of liquid nitrogen is 158 cms. of Hg so that pressures between 15 and 70 cms. of Hg. are in the useful range of relative pressures of from 0.1 to 0.4.

Measurements of the surface areas of catalysts are important for several reasons. In the first place, they indicate the extent to which varying activity may be attributed to changes in surface areas. Secondly, the area values provide a means for determining whether promoters and supports improve catalysts by increasing or maintaining area or by qualitative changes that increase catalyst activity per unit surface area.

For example, two catalysts of widely different areas may show the same activity per unit bulk or reactor volume or per unit mass. It is then essential to know the area difference because of the significance of the surface composition of the low area catalyst. Provided

the surfaces of the two catalysts have the same relative accessibility, the surface of the low-area catalyst is qualitatively superior, as demonstrated by its greater activity per unit area (specific activity). It is also important to study the catalyst of greater area with respect to the preparation techniques responsible for the high area structure. It should thus be possible to combine this knowledge and incorporate the superior chemical or promoter composition in the structure of greater surface. The ultimate objective of such studies is to obtain a thermally stable catalyst of optimum specific activity and area.

It has been shown that the surface area of a catalyst for the Fischer Tropsch reaction is a measure of the activity. However, in J. Roxburgh⁽²¹⁾ investigation, he indicated that the surface area is not a controlling factor, but it is assumed that a certain minimum area is necessary for an efficient catalyst.

EXPERIMENTAL

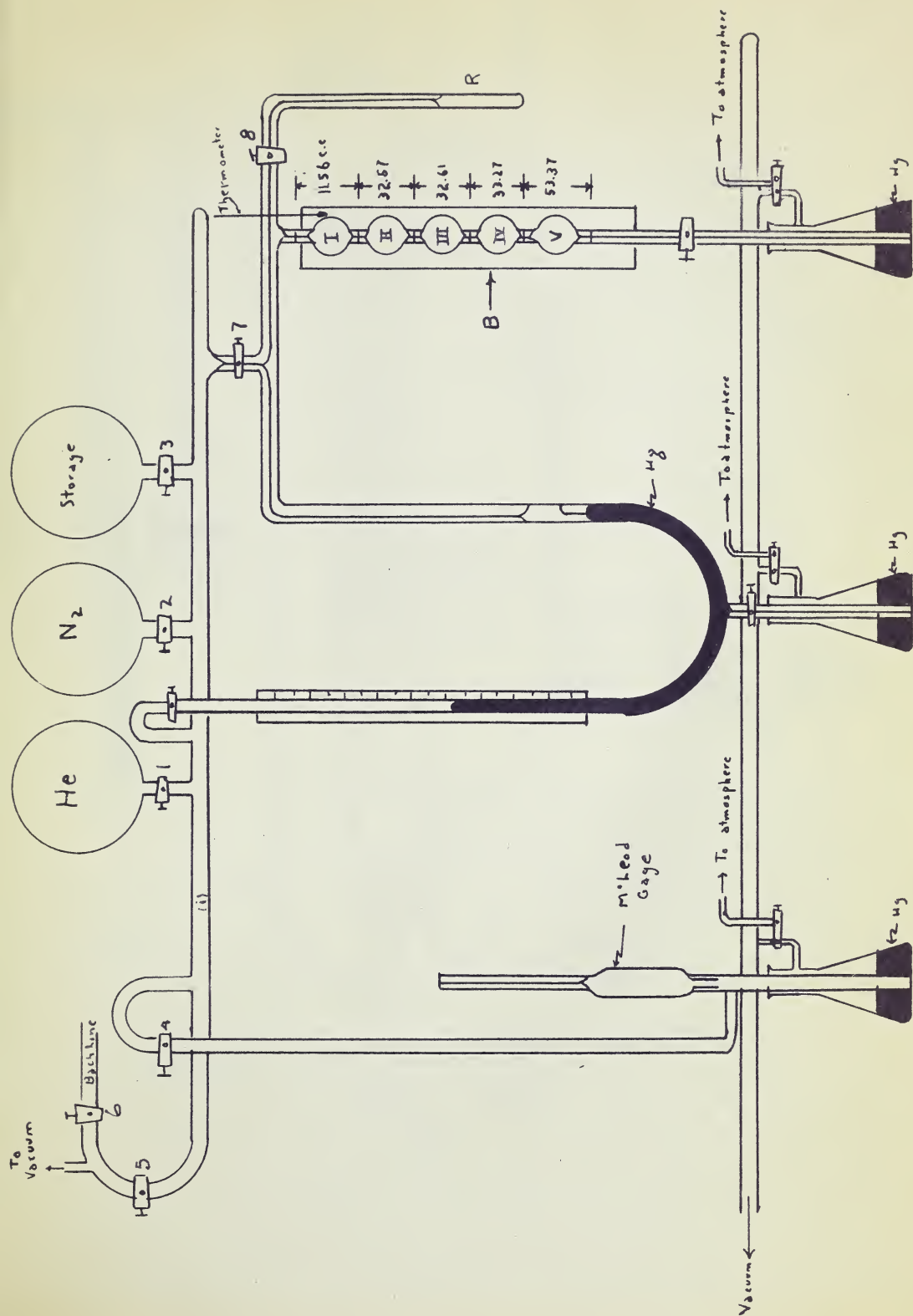
A. Apparatus

The apparatus used was an adaptation of that design first proposed by Bamet for the study of adsorption. This is shown in Fig. 3. Storage bulbs A-B-C for the gases used in these measurements were connected by stopcocks, 1,2,3, to a vacuum line. This was connected through a stopcock, 4, to a McLeod Gauge, and through stopcock 5 to a mercury diffusion pump backed by a rotary oil pump. Through stopcock 5 the line, (1), was connected to the vacuum line and the gas storage bulbs. A mercury manometer, which could be evacuated through stopcocks 5 and 7 was used to measure the pressure in this part of the system. A series of bulbs of known volume, I, II, III, IV, V, and the reaction chamber, R, (which could be surrounded by an electric furnace or a vacuum flash), were connected to this manometer.

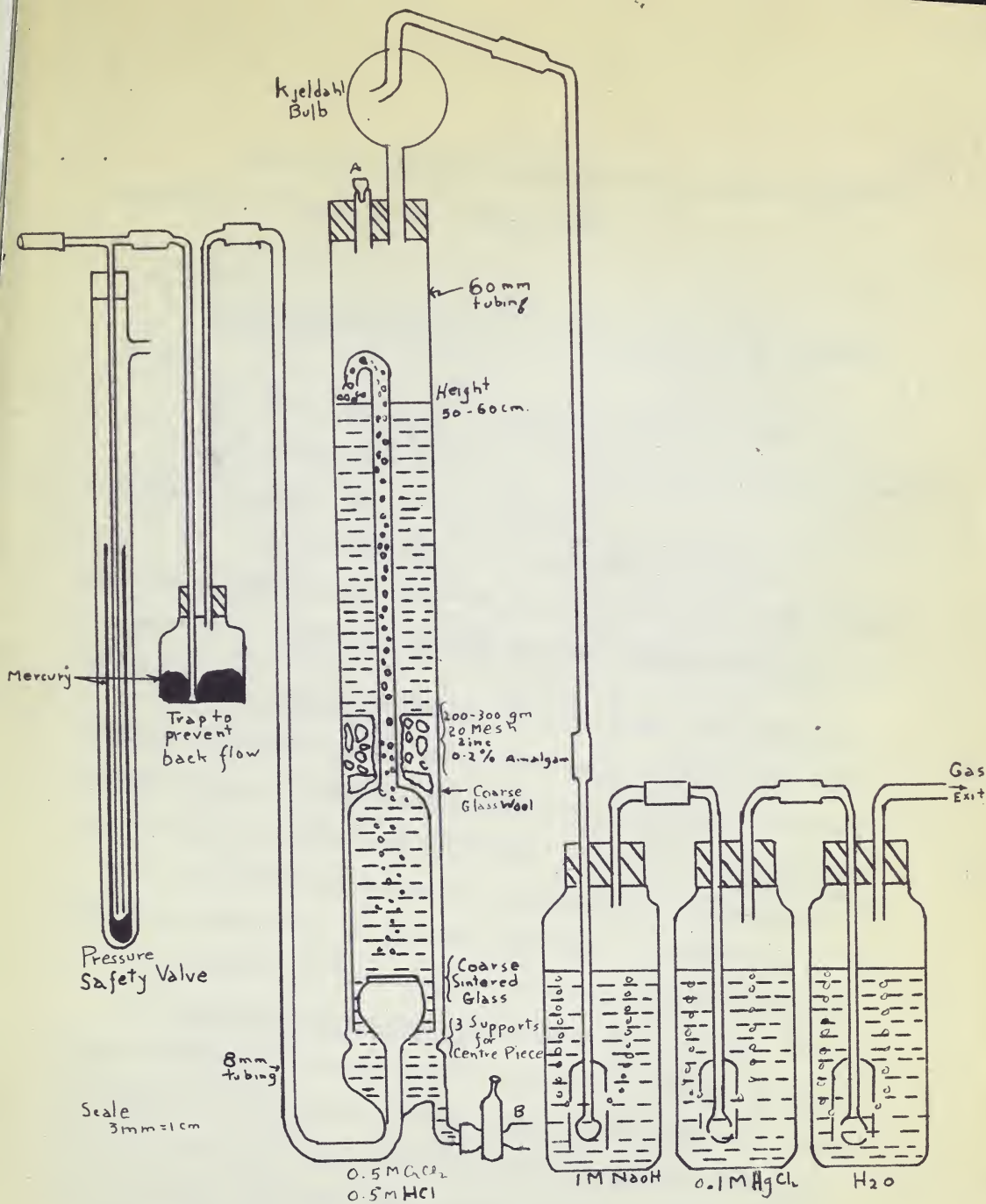
The volume of the line from the manometer to stopcocks 7 and 8, and the calibrated volumes, were calibrated, so that with the mercury level at known points between the bulbs, the volume of the system was accurately known.

B. Preparation of Gases

The gases used were nitrogen and helium. Nitrogen was tank nitrogen passed through a solution of CrCl_2 , Fig. 4, to remove traces of oxygen. The CrCl_3 thus formed was reduced to CrCl_2 by granular zinc. The nitrogen was then passed through Na_2CO_3 , P_2O_5 and CaCl_2 to remove any moisture. As a final precaution against any condensable gases and vapors the nitrogen was passed through a liquid air trap.



Apparatus for finding Surface Area.
Fig. 3



SYSTEM FOR REMOVING OXYGEN
FROM GASES

Fig. 4

Helium was commercial helium passed through an activated charcoal scrubber immersed in liquid air.

C. Procedure

i. Preparation of Catalyst⁽¹⁰⁾ --The composition of catalyst

'C' was:

Co : ThO₂ : MgO : Bentonite -- 100 : 6 : 12 : 200

It was prepared by the rapid simultaneous mixing of boiling solutions of cobalt and thorium nitrates.

40 grams Cobalt, 2.4 grams ThO₂ per litre and sodium carbonate (88 grams Na₂CO₃ per litre) and a warm aqueous suspension of magnesia and bentonite (both passed through 72 mesh B.S.S.).

The mixture was boiled for two minutes with vigorous stirring, filtered rapidly, and the precipitate washed free from occluded salts with boiling distilled water. The filter cake was dried in air at 110°C. and graded into 7 - 14 B.S.S. granules.

To aid in pelleting the catalyst, the dried catalyst was ground and mixed with 5 per cent graphite. The granulated or the pelleted catalyst was then ready to be charged into the test unit.

ii. Preparation of the Sample--A weighed sample of the catalyst to be tested was put in the chamber and the whole sealed in place. The sample was degassed at 100°C. until the pressure would remain at less than 1×10^{-3} mm. of mercury, with the mercury diffusion pump shut off. This step took approximately one hour.

iii. Measurement of the Dead Space--The system was completely evacuated and a measured amount of helium was admitted through the charcoal scrubber into Bulb 2. With the stopcocks closed the pressure on the manometer was noted. The temperature of the water bath was recorded.

The 'dead space' around the adsorbent sample up to stopcock 7 was determined using the purified helium. To make this dead space determination a volume of purified helium was admitted into the burette B, the stopcock 8 being closed. The volume of this helium was measured with the calibrated burette and manometer. After having placed the desired cold bath around the sample bulb, (cracked ice at $0^{\circ}\text{C}.$), the stopcock, B, was opened and the volume of helium left in the burette at equilibrium was determined. The difference between the original volume of helium and that left in the burette was the volume required to fill the 'dead space' to the observed pressure. Such a calibration assumed, of course, that helium was not adsorbed but merely filled the space surrounding the adsorbent. The assumption was justified, because at adsorption temperatures of $0^{\circ}\text{C}.$ the adsorption of helium on all nonporous, and most porous adsorbents would always be very small compared to that of the adsorbate being used.

Calculation of the 'dead space' was made as follows:

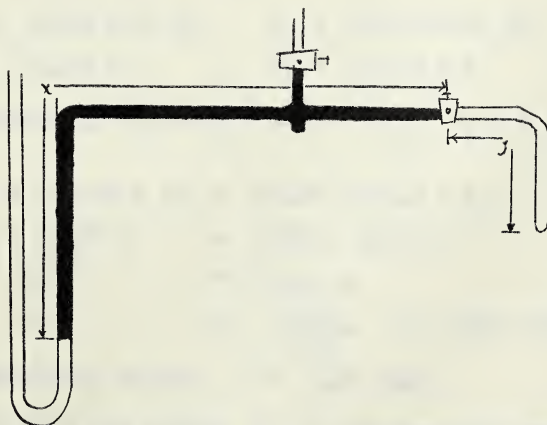


Fig. 5

$$P_1 (V_1 + x) = P_2 (V_2 + x)$$

$$x = \frac{P_2 V_2 - P_1 V_1}{P_1 - P_2}$$

where x = the volume of the shaded area shown in Fig. 5
 P_1 = pressure in bulbs at one volume
 P_2 = pressure in bulbs at second volume
 V_1 = volume corresponding to P_1
 V_2 = volume corresponding to P_2

After x was determined the volume of the dead air space was found in a similar manner, the catalyst chamber being immersed in a thermos flash, containing cracked ice.

The calculation was made as follows:

$$P_1 \left(\frac{V_1 + x}{T_1} + \frac{y}{273} \right) = P_2 \left(\frac{V_2 + x}{T_1} + \frac{y}{273} \right)$$

where T_1 = temperature of water jacket around calibrated bulbs
 y = volume of dead air space as shown in Fig. 5

A sample calculation for both x and y is shown:

$$\begin{array}{ll} P_1 = 33.82 \text{ cms. Hg} & P_2 = 56.26 \text{ cms. Hg} \\ V_1 = 76.74 + x & V_2 = 44.13 + x \end{array}$$

$$\text{Therefore, } P_1 (V_1 + x) = P_2 (V_2 + x)$$

$$33.82 x (76.74 + x) = 56.26 (44.13 + x)$$

$$2595 + 33.82 x = 2483 + 56.26 x$$

$$113 = 22.44 x$$

$$x = \frac{1130}{224} = 5.04 \text{ ccs.}$$

$$\text{Therefore, volume } x = 5.04 \text{ ccs.}$$

To find the volume y of the dead air space using He at 0°C :

$$\begin{aligned} P_1 &= 24.84 \\ V_1 &= \frac{81.77}{295.6} + \frac{y}{273} \end{aligned}$$

$$\begin{aligned} P_2 &= 40.36 \\ V_2 &= \frac{49.16}{295.6} + \frac{y}{273} \end{aligned}$$

$$P_1 V_1 = P_2 V_2$$

$$24.84 \left(\frac{81.77}{295.6} + \frac{y}{273} \right) = 40.36 \left(\frac{49.16}{295.6} + \frac{y}{273} \right)$$

$$24.84 (.2767 + .00366 y) = 40.36 (.1663 + .00366 y)$$

$$6.873 + .0909 y = 6.712 + .1477 y$$

$$y = \frac{.0161}{.0568} = 2.83$$

Therefore, volume of dead air space 'y' = 2.83 ccs.

The deviation of helium from the perfect gas law is negligible even at 83°K.

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RESULTS AND DISCUSSION

A. Determination of Surface Area

The catalyst was again degassed at 100°C until a vacuum of at least 0.001 mm. of mercury could be maintained with the mercury vapor pump shut off.

Stopcock 5 was closed and the catalyst chamber was immersed in liquid air. A measured amount of nitrogen was taken in bulbs B by opening stopcocks 2 and 7. With these stopcocks closed again the pressure and temperature of the gas in the bulbs was recorded.

Stopcock B was opened and the new pressure recorded. The mercury level was varied in bulbs B to give several known volumes with corresponding pressures between 15 and 75 cms. of mercury.

V_B is the volume of the bulbs and line containing N_2

P_B is the pressure in cms. of mercury.

T_B is the temperature of the gas.

V_b is the known volume of bulbs and line to stopcock 10.

P_b is the pressure with stopcock 10 open.

V_h^o = volume of gas in catalyst chamber at S.T.P.

V_b^o = volume of adsorbate remaining at time of measurement
--corrected to S.T.P.

ΔV_a = volume gas adsorbed

$$= V_B^o - V_B^o - V_h^o \quad (\text{reduced to S.T.P.})$$

$$V_b^o = \frac{P_B V_B \times 273}{T \times 760}$$

$$V_b^o = \frac{P_b V_b \times 273}{T \times 760}$$

$$V_h^o = \frac{V_h (1 + \alpha)}{76} \times \frac{273}{83} \times P_b$$

where V_h = volume of helium required to fill the dead space to the pressure P_b of the experiment; α = correction factor to take into account the gas imperfection of the adsorbate at the temperature of the cold bath. α for N_2 at $-190^\circ A$.

$$= .0455.$$

Then $\frac{P_b}{P_0}$ and $\frac{P_b}{\frac{V_a^o}{gm.} (P_0 - P_b)}$ were calculated and

plotted against one another. From the B.E.T. equation the slope of this plot is $\frac{(C-1)}{V_m C}$ and the intercept is $\frac{1}{V_m C}$. Then

$$V_m = \frac{1}{a + b}, \text{ where 'a' is the slope and 'b' the intercept.}$$

From V_m the surface area was calculated, assuming the area of the liquid nitrogen molecule to be $16.6^\circ A$.

$$\text{Surface Area} = \frac{V_m \times 6.02 \times 10^{23} \times 16.6 \times 10^{-16}}{22,400 \times 10^4}$$

The units of surface area

$$\begin{aligned} &= \frac{\text{ccs.}}{\text{gm.}} \times \frac{\text{no mol.}}{\text{mol.}} \times \frac{\text{cm}^2}{\text{ccs.}} \text{ mol.} \\ &= \frac{\text{cms}^2}{\text{gm.}} = \frac{\text{square metres}}{\text{gm.}} \end{aligned}$$

A sample calculation is shown in Table I, (for Catalyst 'C').

B. Measurement of Adsorption

The procedure was identical with that described for the determination of the surface area. Calculations were carried only as far as ΔV_a .

TABLE I CATALYST "C"

Run #	T _B	P _B	P _b	V _B	V _B ^o	V _b ^o	V _A ^o	V _n ^o	ΔV _a	V _a	$\frac{V_a}{C_m.}$	$\frac{P_b}{V_a}$	Po-Pb	$\frac{P_b}{V_a(Po-P_b)}$	$\frac{P_b}{P_o}$
1	22.6	19.32	11.07	168.60	39.72	22.7		.653	16.35	16.35	17.00	.650	146.93	.00443	.070
2	23.0	16.37	15.25	115.23	22.92	21.40	.653	1.348	.17	16.52	17.20	.886	142.75	.00621	.0965
3	23.2	21.62	20.05	81.96	21.43	19.90	1.348	2.32	-.79	15.73	16.35	1.225	137.95	.00890	.127
4	23.6	33.07	29.08	49.35	19.60	17.38	2.32	4.73	-2.51	13.22	13.78	2.117	128.92	.0158	.184

Catalyst # C Sample = .9605 gms.

Volume from bulb to manometer = 5.22 ccs.

Volume of dead air space = 1.30 ccs.

TABLE 2 SURFACE AREA OF BENTONITE

Run #	T _B	P _B	P _b	V _B	V _B ^o	V _b ^o	V _H ^o	V _h ^o	ΔV _a	V _a	V _a Gm.	Pb Va	Po-Pb	$\frac{Pb}{Va(Po-Pb)}$	Pb Po	Time min.
1	24.6	17.27	6.45	168.60	35.20	13.14	.464	21.60	21.60	30.90	.209	151.55	.00138	.0408	.0408	20
2	25.0	9.37	7.69	115.23	13.02	10.68	.464	.714	1.63	23.23	33.29	.231	150.31	.00154	.0468	8
3	25.2	10.77	8.77	81.96	10.58	8.63	.714	.915	1.03	24.26	34.78	.254	149.23	.00170	.0550	8
4	25.4	14.57	10.37	49.35	8.65	6.15	.915	1.43	1.07	25.33	36.20	.286	147.63	.00194	.0657	9
5	25.6	30.37	12.57	16.78	6.13	2.54	1.45	1.72	2.16	27.49	39.39	.319	145.43	.00219	.0795	7
6	25.8	39.92	12.52	5.22	2.50	.785	1.88	1.88	-.17	27.32	39.00	.321	145.48	.00220	.0794	7

Bentonite Carrier # RL769

Volume from bulb to manometer = 5.22 ccs.

Volume of dead air space = 1.59 ccs.

Weight of Catalyst = .6996 gms.

Surface Areas--The surface areas of catalyst 'C' (Co : ThO₂ : MgO : Bentonite -- 100 : 6 : 12 : 200) and of the Bentonite carrier were measured. The results are shown in Tables I and II and Figures 6 and 7.

Comparing the yields obtained with the various surface areas of the catalysts containing different carriers, we find that the catalyst containing the bentonite carrier may have a better activity than the others. It is, therefore, apparent that the best support for a catalyst would most probably be bentonite because of its larger surface area.

The composition, average run, yield in gm./cu.metre, surface area, are shown in Table III.

(8)

TABLE III

COMPARISON OF BEHAVIOUR OF BENTONITE FILTERCEL CATALYSTS

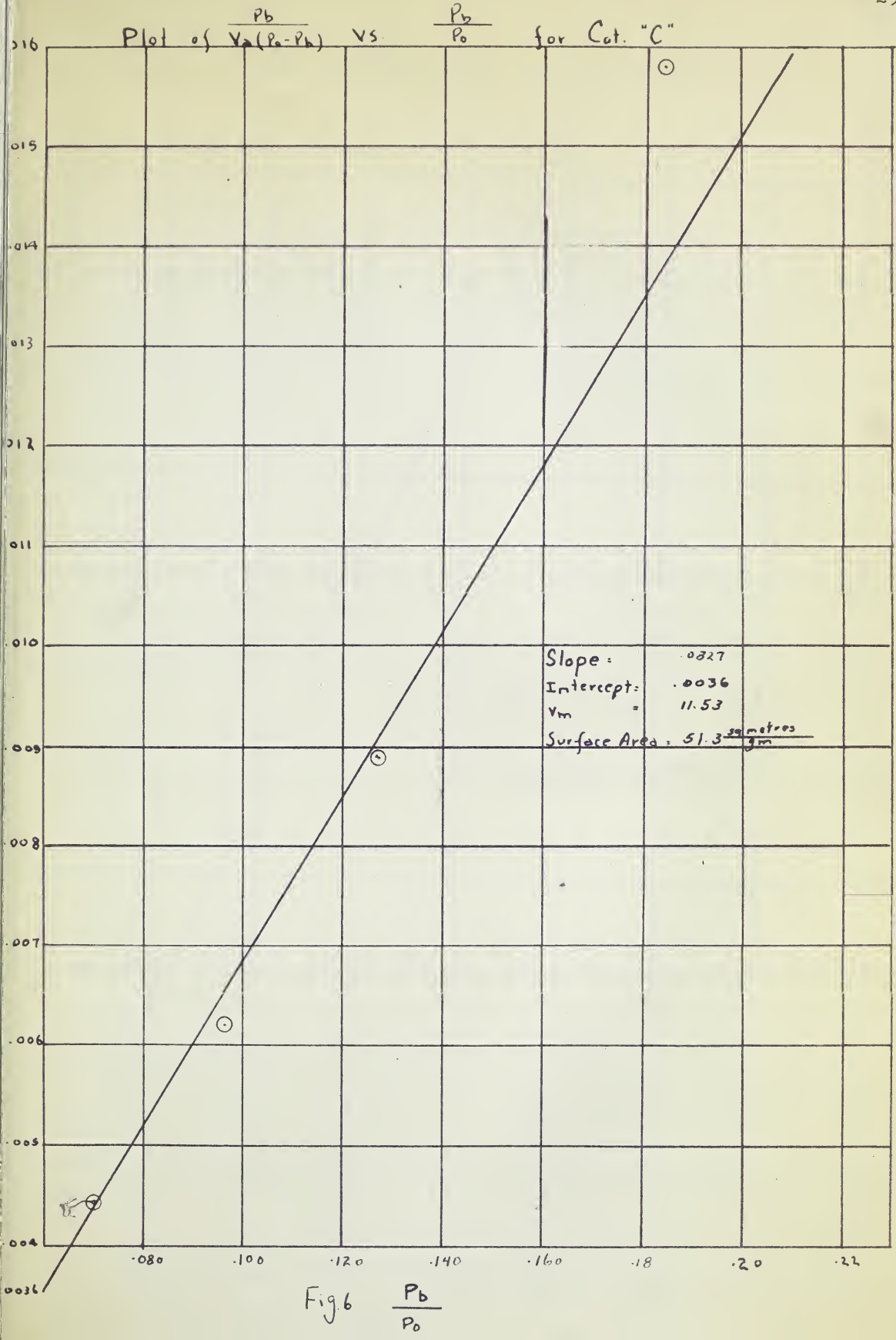
Cat. #	Composition			Average Run	Yield gm. cu M.	Surface Area
7	Co : ThO ₂ : MgO :	Filtercel		Total: 1055 hrs. 94 hours	76	185
	100 : 6 : 12 :	200				
	8	Co : ThO ₂ : MgO :	Filtercel (pelleted with 5 % graphite)		95 hours	82
100 : 6 : 12 :		200				
9		Co : ThO ₂ : MgO :	Bentonite (pelleted with 5 % graphite)		Total: 1822 hrs. 96 hours	90
	100 : 6 : 12 :	200				

TABLE 4

COMPARISON OF SURFACE AREAS OF VARIOUS CARRIERS

<u>Carrier</u>	<u>Surface Area</u> <u>sq.metres/gm.</u>
Bentonite	191
Hiflo Supercel	1.7
Super Floss	2.7
Filtercel	22.7

Figure 8 shows a typical isotherm for the adsorption of N_2 . Example shown is on bentonite at $83^\circ K$. It can be seen that this adsorption is of Type II.



Plot of $\frac{P_b}{P_0}$ vs. $\frac{P_b}{V_0(P_0 - P_b)}$ for Bentonite Carrier

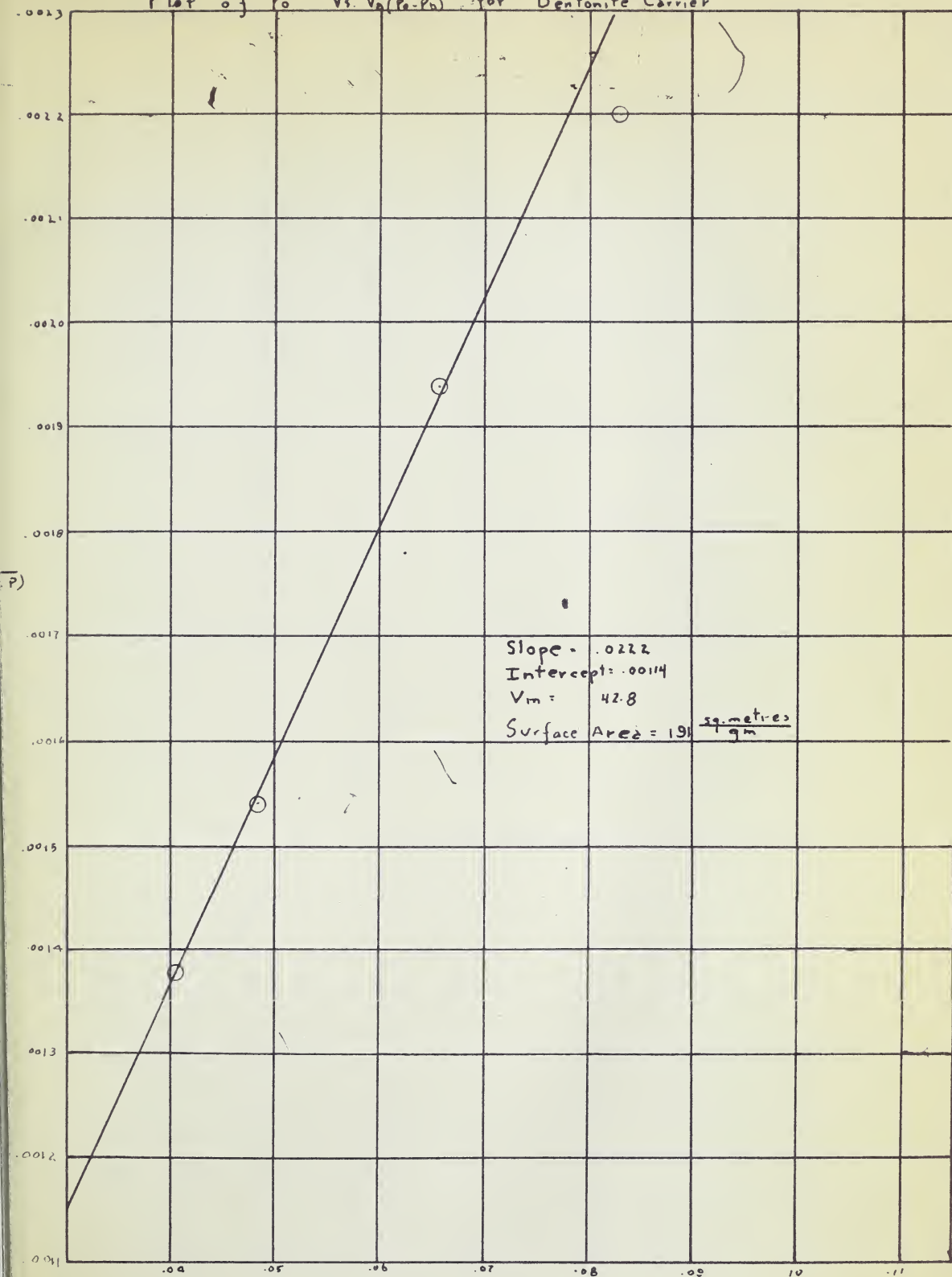
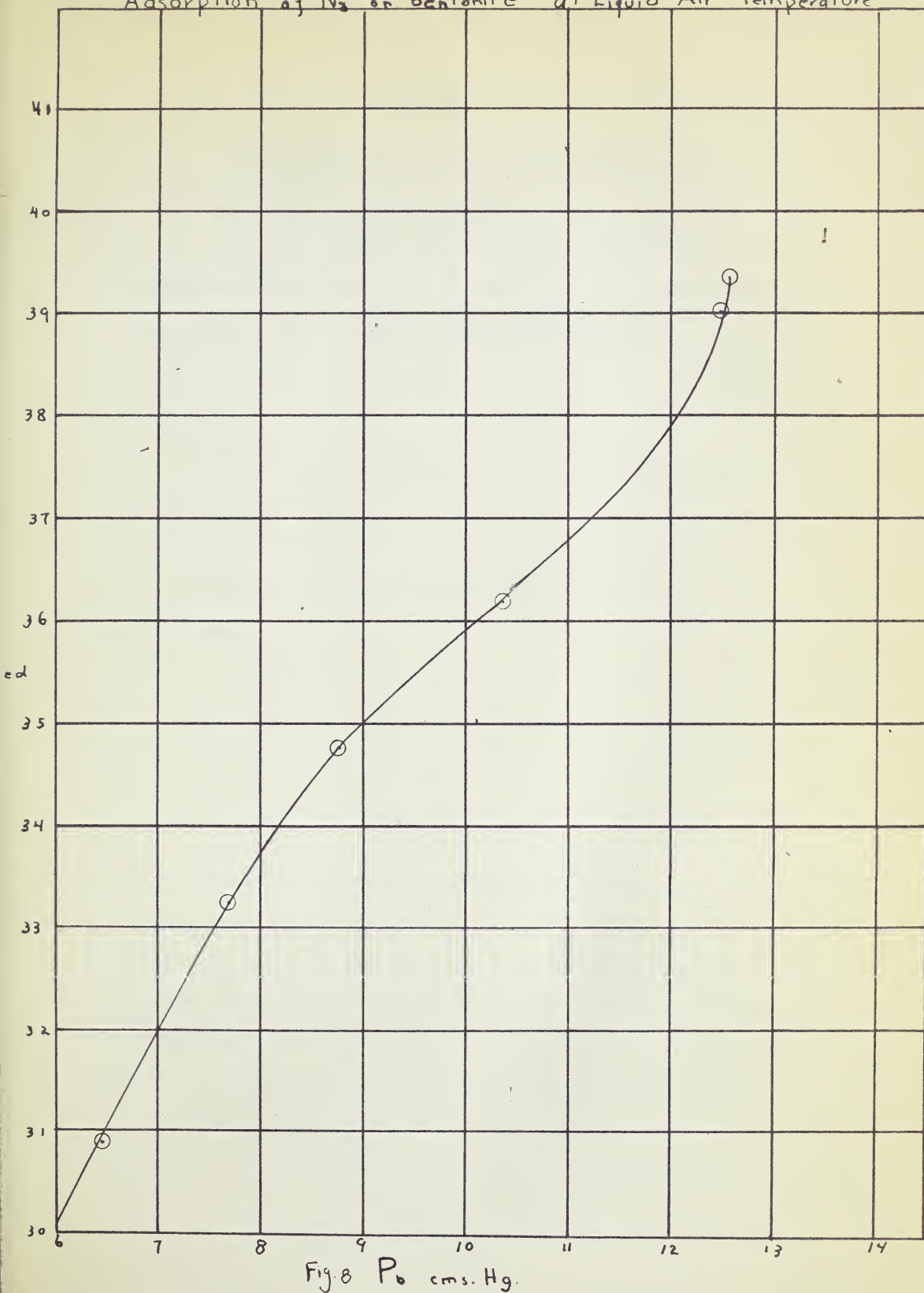


Fig. 7. $\frac{P_b}{P_0}$

Adsorption of N_2 on Bentonite at Liquid Air Temperature

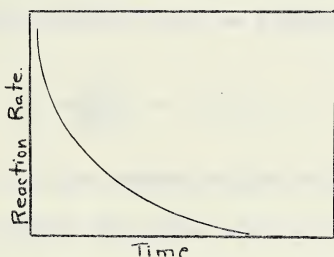
SUMMARY

The surface areas of a bentonite carrier and a CO : ThO₂ : Mg : bentonite catalyst were determined to be 191 and 51 square metres per gram, respectively. The values obtained for the catalyst were of the same order as those reported for similar types of catalysts.

PART II

DECOMPOSITION OF METHANOL FORMIC ACID
AND ETHYL ALCOHOL OVER A FISCHER TROPSCH CATALYSTA. Order of Reaction⁽⁹⁾

Since the rate of a chemical change is proportional to the concentrations of the reacting substances, it is evident that the speed of the process must fall off as the reaction proceeds, for the reactants are being continuously consumed. The change of reaction rate with time must be represented by a curve similar to that shown in Fig. 1, below:



Change of the Rate of Reaction with Time

Fig. 1

The reaction decreases with time in a function which becomes asymptotic with the time axis. It is obviously not a simple matter to define the general rate of a reaction, and so in practice the velocity is considered at a particular instant. In this way valuable results can be obtained. In the study of chemical kinetics reactions are divided into classes determined either by

molecularity, that is, by the number of atoms or molecules taking part in each act leading to chemical reaction, or by the order of the reaction, that is, the number of atoms or molecules whose concentrations determine the velocity, or kinetics, of the process.

Reactions may be classified kinetically as being either homogeneous or heterogeneous. A reaction is said to be kinetically homogeneous if it takes place in one phase only. If two or more phases are involved in the process as in a gaseous reaction proceeding on the surface of a solid catalyst or on the walls of the container, the reaction is said to be heterogeneous.

Reactions of the First Order--In a first-order reaction the rate is directly proportional to the concentration of the reacting substance. The condition can be expressed mathematically in the form:

$$- \frac{dc}{dt} = k c \quad (1)$$

where c is the concentration of the reacting substance, for this equation states that the rate of disappearance of the reactant at any instant is proportional to its concentration at that instant. If a is the initial concentration of the reacting species, and x is the decrease after the lapse of time t , the concentration remaining will then be $(a-x)$; the reaction velocity can be obtained by substituting $(a-x)$ for c in (1); thus,

$$- \frac{d(a-x)}{dt} = k(a-x)$$

or

$$\frac{dx}{dt} = k(a-x) \quad (2)$$

The quantity $\frac{dx}{dt}$, which is a measure of the rate of decomposition is called the reaction velocity, and the proportionality constant k is referred to as the velocity constant, the velocity coefficient, or sometimes as the specific rate. The reaction velocity at any instant is thus equal to the product of the velocity coefficient which is constant at a definite temperature for the given reaction, and the concentration of the reactant at that instant. In order to see how the velocity constant may be evaluated, it is necessary to integrate (2) in the form,

$$\frac{dx}{(a-x)} = k dt$$

remembering that when t is 0, that is, at the beginning of the reaction, the amount x is 0, whereas after time t it is x , the result is:

$$k = \frac{1}{t} \ln \frac{a}{a-x} = \frac{2.303}{t} \log \frac{a}{a-x} \quad (3)$$

An alternate method for testing equation (3) is a graphical one. Equation (3) may be rearranged to the form:

$$\begin{aligned} \ln (a-x) &= -kt + \ln a \\ \log_{10} (a-x) &= \left(\frac{-k_1}{2.303} \right) t + \log_{10} a \end{aligned} \quad (4)$$

Since for any one experiment a is constant, equation (4) is the equation of straight line when $\log (a-x)$ is plotted against t . In such a plot the 'y' intercept will be $\log_{10} a$ while the slope will be $\left(-k_1/2.303 \right)$. Consequently, when a $\log (a-x)$ versus t plot constructed from the experimental data is found to be linear, the reaction is first order.

By taking the slope of the line, k_1 follows as:

$$k_1 = -2.303 (\text{slope})$$

B. Effect of Temperature on Reaction Velocity ⁽¹⁹⁾

Arrhenius first pointed out that the variation of rate constants with temperature can be represented by an equation similar to that used for equilibrium constants, namely:

$$\frac{d \ln k}{dt} = \frac{\Delta E^*}{RT^2} \quad (5)$$

In this Arrhenius equation k is the reaction rate constant; T the absolute temperature; R the gas constant in calories; and ΔE^* a quantity characteristic of the reaction with the dimension of an energy. ΔE^* is known as the energy of activation and plays a very important role in chemical kinetics.

Integrating equation (5) and assuming that ΔE^* is a constant we obtain:

$$\begin{aligned} \ln k &= -\frac{\Delta E^*}{RT} + C \\ \text{or } \log_{10} k &= \left(\frac{-\Delta E^*}{2.303 R} \right) \frac{1}{T} + C \end{aligned}$$

where C^1 and C are constants of integration. However, if the integration is carried out between the limits $k = k_1$ at $T = T_1$ and $k = k_2$ at $T = T_2$, then

$$\log_{10} \frac{k_2}{k_1} = \frac{\Delta E^*}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \quad (6)$$

From equation (6) it is evident that as soon as two different temperatures and two different values of k are available

ΔE^* may be evaluated; or when ΔE^* and a value of k at some one temperature are known, k at another temperature may be calculated.

Equation (5) as a plot of $\log_{10} k$ against $\frac{1}{T}$ should be a straight line with

$$\text{slope} = \frac{-\Delta E^*}{2.303 R} = \frac{\Delta E^*}{4.58} \quad (7)$$

and y intercept equal to C. Consequently if such a plot is constructed and is found to be linear, the equation is confirmed. Further by taking the slope of the line, ΔE^* may be calculated readily through equation (7).

C. The Energy of Activation

In reactions involving two or more molecules it is logical to presuppose that before reaction can take place the molecules must come in contact with each other; in other words, they must collide. If collision is a sufficient cause for reaction, the rate of reaction should equal the rate of collision. However, when the number of molecules actually reacting in a gaseous reaction, as obtained from the observed velocity constants, is compared with the total number of molecules colliding, calculated from kinetic theory, the latter are found to exceed the number undergoing transformation by many powers of ten. This discrepancy can be explained only by the assumption that molecules, in order to react, must be in some special configuration at collision, or that they must be in some exceptionally high energy state, or both. Although configuration does play a part in certain reactions, the appearance of the ΔE^* term in the Arrhenius equation and other considerations definitely favor an exceptional energy state as a prime requisite for reaction; that is, the molecules must be activated before they can react on collision.

According to the concept of activation reactants do not pass directly to products, but must first acquire sufficient energy to pass over an activation 'energy barrier'. The ideas involved can be made clear with the aid of Fig. 2.

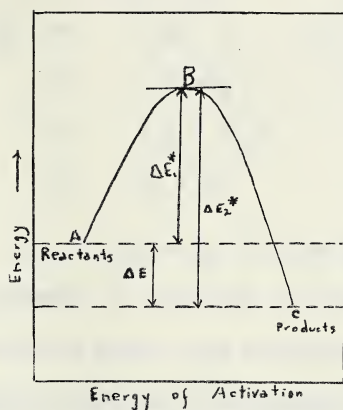


Fig. 2

In this figure A represents the average energy of the reactants; C that of the products; and B the minimum energy which the reactants must possess in order to react. Molecules existing in state B are said to be activated or in an activated state. Since molecules must be activated before reaction, the reaction must proceed from A to C, not directly but along path A.B.C. In other words, molecules must first climb the energy barrier before they can roll down the hill to form products.

The energy that the reactants at A must absorb in order to become activated and react is the energy of activation ΔE^* , of the process $A \rightarrow C$.

This energy is obviously $\Delta E^* = E_B - E_A$, that is, the difference in energy between the activated state and that corresponding to the average energy of the reactants. By the same

argument it can be seen that the energy of activation ΔE_2^* , of the reverse process $C \longrightarrow A$ must be $\Delta E_2^* = E_B - E_C$. From these two activation energies the difference, ΔE , between ΔE_1^* and ΔE_2^* , follows as:

$$\begin{aligned}\Delta E &= \Delta E_1^* - \Delta E_2^* \\ &= (E_B - E_A) - (E_B - E_C) \\ &= E_B - E_A + \quad - E_B + E_C \\ &= E_C - E_A\end{aligned}$$

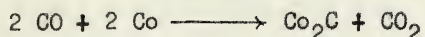
But $\Delta E = E_C - E_A$ is the difference in energy between reactants and products, or the heat of reaction at constant volume. This must mean that in going from the activated state to the products the molecules give up not only the energy absorbed on activation from A to B, but also the energy ΔE corresponding to the difference in energy levels of C and A. Hence it may be concluded that the thermodynamic relations between energies of products are in no way violated by the concept of an activation energy. All it does is to introduce two quantities such that their difference always leads to the heat of reaction. At the same time it is evident that no information can be obtained from heats of reaction without the aid of kinetic study or other considerations.

D. The Mechanism of the Synthesis Reaction

Experiments on the rates of formation and reduction of cobalt carbide on cobalt-thoria-kieselguhr catalysts under various conditions indicate that the first step of the synthesis gases with the catalyst give cobalt carbide.⁽⁷⁾ When this is reduced by chemisorbed hydrogen atoms only methane is formed. Reduction by molecular Hydrogen, however, leads to the formation of longer chain hydrocarbons. Hence, in order to obtain oils, the conditions of

the synthesis have to be adjusted so that only very few chemisorbed hydrogen atoms are present on the catalyst surface.

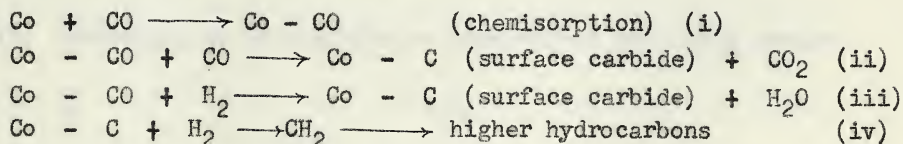
It is significant that the three metals, cobalt, nickel and iron, which show activity as Fischer catalysts at atmospheric pressure, all react at 200°C . with carbon monoxide to form carbides. Fischer postulated that such carbides are intermediate compounds in the synthesis. Bohr and Jessen found that precipitated and reduced cobalt reacted smoothly at 230°C . with carbon monoxide as follows:



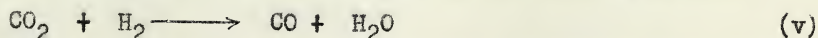
At higher temperatures the carbide becomes unstable and free carbon is formed as well.

Mechanism of the Synthesis of Hydrocarbons from Carbon Monoxide

and Hydrogen--During the synthesis the catalyst is in contact with both hydrogen and carbon monoxide, and the formation and utilization of the carbide can be envisaged as follows:



The oxygenated product of the Fischer synthesis over a cobalt catalyst is water and not carbon dioxide, a fact which suggests that (iii) proceeds more rapidly than (ii) for it is impossible that the water could be produced by the water-gas shift reaction.

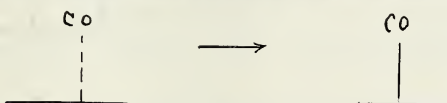


since at 200°C the equilibrium concentration of water vapor would be extremely small. This fact together with other evidence, indicates that in the synthesis of hydrocarbons the Fischer catalyst must be inactive for the water gas shift reaction although normally it is a most effective catalyst for it.

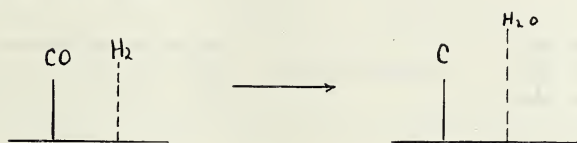
In more detail the mechanism of the Fischer synthesis

involves the following reactions. These reactions may be depicted as follows, where ---X represents a chemisorbed radicle X, and -----Y represents a molecule Y adsorbed by Van der Waal's forces.

(i) Chemisorption of carbon monoxide:



(ii) Reduction of chemisorbed carbon monoxide by hydrogen to give carbide:

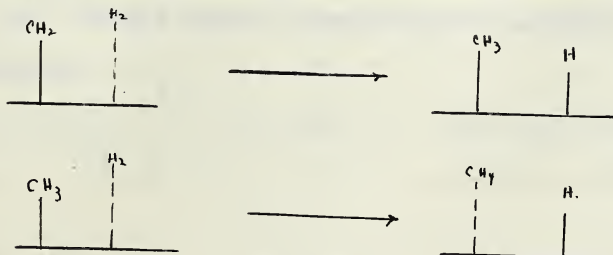


(iii) Reduction of the carbide to chemisorbed methylene groups:

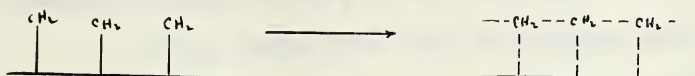


If at this stage there is a large amount of chemisorbed hydrogen on the catalyst surface, the next step is:

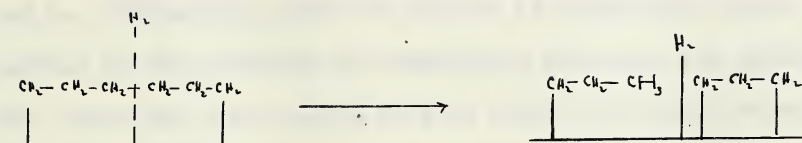
(iv) - a.



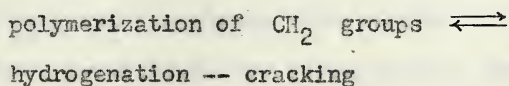
and methane is the product; but if, on the other hand, only a little chemisorbed hydrogen can be present, association of the methylene groups occurs to give macro molecules:



(iv) - b. These macro molecules are then disrupted by interaction with hydrogen, probably as:

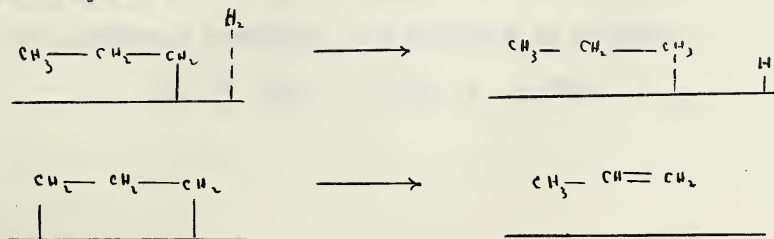


and the chain length of the products obtained will depend on the amount of hydrogen available for this process, which is given by the amount of chemisorbed hydrogen present on the surface. If much hydrogen is available, the equilibrium



is pushed over to the right hand side and hydrocarbons of small chain length are formed, and vice versa.

(v) Finally there is desorption of paraffins or olefins, probably as:



The normal initial period, when methane is being formed before the synthesis of oil sets in, is easily understandable on this basis, because the experimental evidence is that during the first few hours after admission of synthesis gas to the catalyst, carbide is being slowly built up.

Since, during this time the catalyst will be incompletely covered with carbide and chemisorbed hydrogen can therefore be present on its surface, methane will be synthesized; but as less of the surface becomes available for chemisorbed hydrogen, so the formation of methane will diminish and the synthesis of oil set in. Ultimately, when the surface is completely covered with carbide to the exclusion of chemisorbed hydrogen, the synthesis will cease and the catalyst will be choked with heavy waxes as there is no means left for removing them from the surface. Hence revivification in hydrogen must be carried out before the synthesis can continue.

Although no direct evidence that cobalt catalysts are capable of cracking hydrocarbons has been found, Craxford shows that there is an optimum rate of synthesis gas flow over the catalyst bed, and postulates that at slower rates of flow the hydrocarbons produced in the first part of the bed are cracked in the later part to methane with consequent reduced yields. Craxford further shows that the rate of formation of CO_2 steadily drops as the flow of synthesis gas is increased, showing no maximum, so that the formation of CO_2 cannot be connected directly with the synthesis reaction. The reaction is probably:



rather than



The experimental evidence on which Craxford bases this hypothesis is shown in Figure 3 in graphical form:

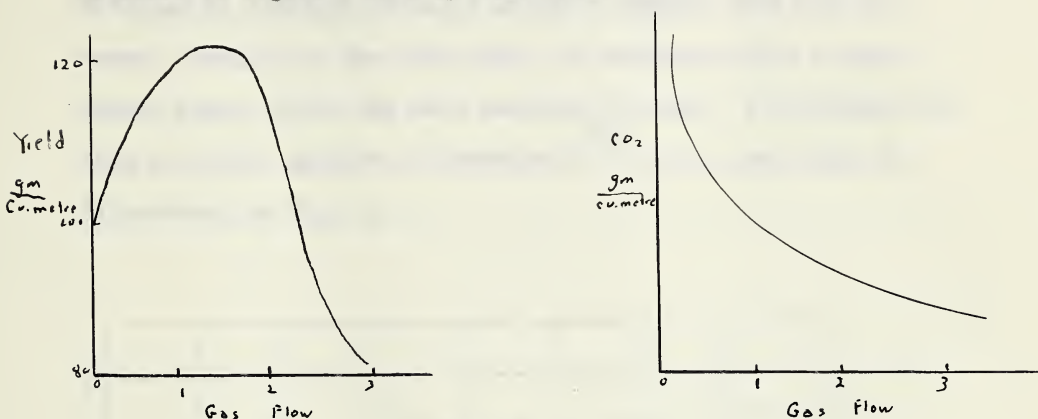


Fig. 3

Litres per Hour per gram of Cobalt

E. Decomposition of Oxygenated Compounds

Unimolecular reactions in gases have a rather exceptional theoretical interest because they involve, apparently, the spontaneous change of isolated molecules. The thermal decomposition of methanol vapor satisfies the experimental criteria of a homogeneous unimolecular reaction.

It will be shown that the decomposition of methanol vapor is a homogeneous reaction which satisfies the chief experimental criterion of a unimolecular change. It should therefore be possible to calculate the unimolecular velocity constants. For this purpose it is essential to know the limiting value of the pressure increase attending the decomposition. It can hardly be expected that the experimentally observed 'end point' would be the proper value for insertion in the unimolecular equation,

because the products formed in the primary decomposition of the methanol undergo slow subsequent reactions, continuing after all the methanol is decomposed. It is, in fact, found that the curve obtained by plotting pressure increase against time does not become parallel to the time axis, but continues with a small upward slope, after the main reaction is over. A correction for this is easily applied, (Hinshelwood⁽¹⁴⁾), in a way which is illustrated in Fig. 4.

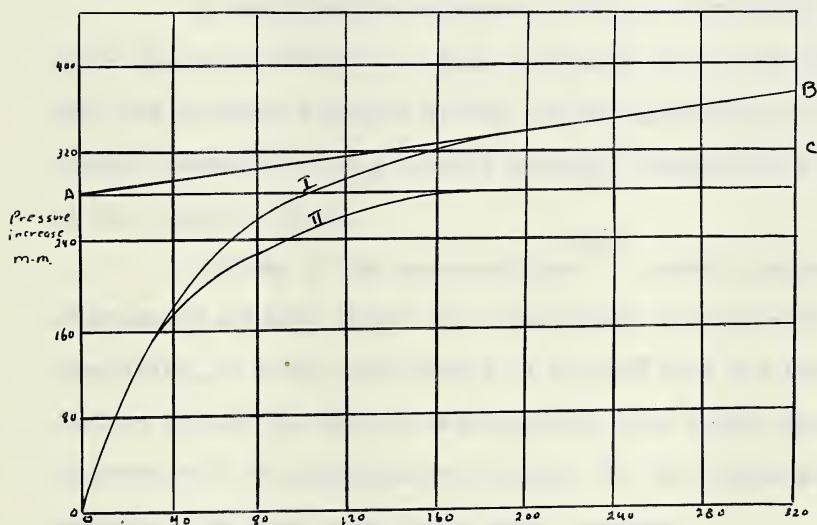


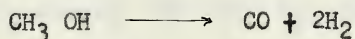
Fig. 4

Curve I is the experimental curve, which does not become quite horizontal in the normal way. The line A.B., to which the curve is asymptotic, is drawn and produced to meet the pressure axis at A. The vertical distance between A.B., and the horizontal line A.C., at any time gives the pressure increase attributed to the subsequent reactions. By subtracting these values from the ordinates of curve I curve II is obtained, which is the ideal

decomposition curve of the methanol and is asymptotic to the horizontal line A.C, which represents the true end point of the reaction.

F. Thermal Decomposition of Methyl Alcohol

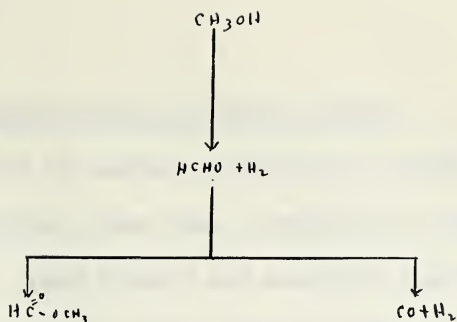
Methyl alcohol decomposes catalytically in the presence of Fischer Tropsch Catalyst to formaldehyde and hydrogen at approximately 185° C. Formaldehyde rapidly decomposes into carbon monoxide and hydrogen so that the resultant equation is:



As formaldehyde undergoes certain condensation reactions which are more prominent at high pressures, it is not surprising that the pressure increase during the decomposition of methyl alcohol decreases as the initial pressure increases and depends on the vessel surface.

A study of the decomposition⁽¹¹⁾ permits operation at atmospheric pressure where the experimental procedure is greatly simplified, it being justifiable to suppose that the catalyst mixture giving the maximum decomposition into carbon monoxide and hydrogen will be particularly suitable for the synthesis of methanol from these same gases under pressure.

The decomposition is a true measure of the activity of the catalysts only when the time of contact and the concentrations are the same in each case. It will be seen at once that the decomposition is by no means a simple reaction, as evidenced by the complexity of the products. Formaldehyde, methyl formate, CO₂ and methane are formed in addition to CO and Hydrogen. The decomposition may be represented tentatively by the following scheme:

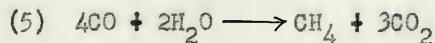
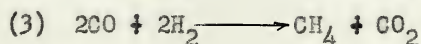


With the Fischer Tropsch Catalyst, that is, Co: ThO₂: MgO : Kieselguhr the methanol decomposes almost completely at 185°- 210°C. forming CO and H₂. These probably react further to form a mixture of liquid hydrocarbons similar in properties to, but smaller in amount than, the mixture obtained directly from water gas over this catalyst. The liquid hydrocarbons formed are secondary products, having been obtained from CO and H₂.

G. The Thermal Decomposition of Ethyl Alcohol

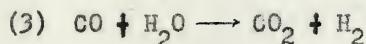
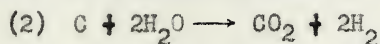
In spite of numerous experimental results the complexity of the reactions prevents more than a qualitative indication of the reaction involved. Many primary and secondary reactions are possible. The nature and course of the reaction depends upon the catalyst, conditions of temperature and space velocity used. Among the gaseous products may be hydrogen, CO , CO_2 , $\text{CH}_2 = \text{CH}_2$, CH_4 and $\text{CH}_3 - \text{CH}_3$. The liberation of carbon is also possible and a few liquids such as water aldehydes, esters and polymerization products can be formed.

The formation of CH_4 during the decomposition may occur in several ways. The primary decomposition of alcohol to aldehyde followed by the decomposition of the aldehyde to methane and carbon monoxide, is probably the most frequent and largest source of methane. The hydrogenation of CO may be mentioned as a second important source. Boomer and Morris believed that several other reactions must be considered in experiments at atmospheric pressure. The reactions that appear worthy of consideration are as follows:



It is possible that any or all of these secondary reactions can be sources of methane. Some such as (1) and (2) may be considered probable and even established by the elimination of others from the range of possibility.

The production of CO_2 during the decomposition of ethyl alcohol may occur through the operation of several reactions. The following secondary reactions may be listed as possibilities as shown by work done elsewhere



Sabatier⁽¹⁴⁾ showed that ethyl alcohol could undergo two important types of decomposition; one to ethylene and water, a reaction promoted chiefly by oxide catalysts, and the other to hydrogen and acetaldehyde promoted chiefly by metals. Many catalysts promote both reactions. Thoria yields approximately equal volumes of ethylene and hydrogen.

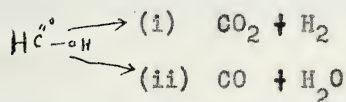
A supported thoria catalyst promotes the ethylene reaction almost exclusively.

Using a $\text{CO} : \text{ThO}_2 : \text{Mg} : \text{Kieselguhr}$ - a partial decomposition
(8A)
of ethyl alcohol takes place proceeding mainly in accordance with the equation



H. The Thermal Decomposition of Formic Acid ⁽¹⁵⁾

The catalytic decomposition of formic acid vapor at the surfaces of metallic oxides can be explained by considering that the reaction takes place in an adsorbed layer one molecule thick, partially covering the catalyst surface. Two alternative modes of decomposition take place on the Fischer Tropsch catalyst, i.e.



APPARATUS

The apparatus used is shown in figure 5. The liquid to be decomposed was stored in bulb II. This bulb could be heated to various temperatures and give various pressures of gaseous reactant in the storage bulb I. Stopcock 2 connects these bulbs to prevent the condensation of reactant in the connecting lines, these and bulb II were maintained at a temperature above the boiling point of the reactant.

A manometer was connected to the storage bulb I and the amount of gas used in a reaction could be determined by readings of this manometer before and after the reaction.

The storage bulb was connected through stopcock 3 to the reaction vessel III by capillary tubing which was also heated. A manometer M was connected to this bulb. This vessel, which contained the catalyst, was surrounded by a furnace which was held at a constant temperature ± 2 degrees by a thermoregulator. The temperature of the reaction vessel was determined by an iron constantan thermocouple.

The whole system could be evacuated through stopcock I (a three-way stopcock) which connected to a mercury diffusion pump and then a hyvac pump.

The gases necessary for carbiding and reducing the catalyst entered the system through stopcock I and left the system through stopcock 4.

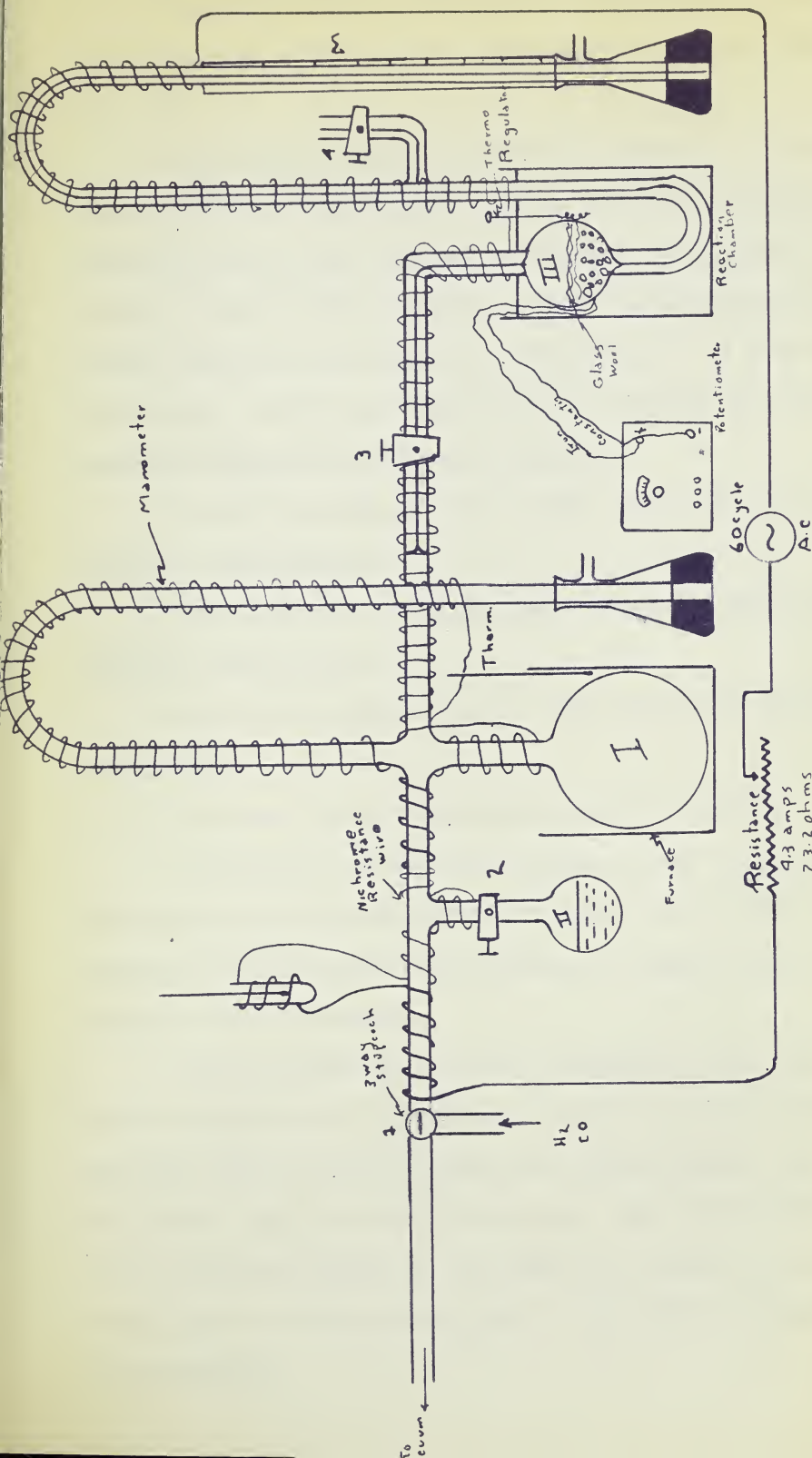


Fig. 5 Apparatus for finding Rates of Decomposition

CHEMICALS

The methyl alcohol used in this investigation was purified according to the following procedure (Fieser: "Experiments in Organic Chemistry", Part II, page 355).

A good grade of methyl alcohol was placed in a large flask provided with an efficient condenser and about 5 - 15 gms. of magnesium turnings was added, the amount being adjusted according to the quantity of water probably present. When the first vigorous reaction was over and the magnesium was largely dissolved, the mixture was refluxed for 2 - 3 hours to complete the dehydration, and the dry alcohol was then distilled from the residue of magnesium hydroxide and magnesium methoxide.

The ethyl alcohol obtained was 98%. This was then purified by fractional distillation.

Formic acid C.P. grade was used. This was further purified by fractional distillation.

Acetone C.P. grade was used. This was further purified by fractional distillation.

The gases used were hydrogen and carbon monoxide.

The hydrogen used was tank hydrogen passed over copper foil at 300°C, then through an activated charcoal trap immersed in liquid air. The only impurity of any account in tank hydrogen is oxygen, which is completely removed by this treatment.

Carbon monoxide was prepared by dropping formic acid (85%) into concentrated sulfuric acid (5 g. 185°C). The gas was passed through dehydrite and soda lime tubes to absorb moisture and carbon dioxide, then through a glass wool packed trap immersed in liquid air. The only impurities present in carbon monoxide prepared in this manner are moisture and acid spray and a small amount of carbon dioxide, all of which will be completely removed by this treatment.

PROCEDURE

Preparation of Sample:

A weighed sample of the catalyst to be tested was put in bulb III and the bulb sealed in place. The sample was degassed at 200°C until a vacuum was obtained and would hold with stopcock 3 shut off. Then purified H_2 at 200°C was passed through stopcock 1 over the catalyst for two hours. Pure carbon monoxide was then passed over the catalyst for an additional six hours - thus activating the catalyst and preparing it for the decomposition of the various substances to be tested.

Determination of the Rates of Decomposition:

The catalyst was again degassed at 200°C until a vacuum could be maintained with the mercury vapor pump shut off. Stopcocks 1 and 3 were shut off thus isolating the system. Stopcock 2 was opened and the methanol in bulb II was heated to boiling. The vapors were stored in bulb I - maintained at 110°C. When a reasonable amount of methanol vapor has accumulated stopcock 2 was shut off and stopcock 3 was opened - admitting methanol vapors to the catalyst chamber at 200°C. Stopcock 3 was then shut and the pressure change on Manometer M with time was recorded.

The reaction of acetone ethanol and methyl alcohol were studied over an oxidized catalyst ("C") at temperatures between 200° - 210°C.

The decomposition of formic acid, ethanol and methanol over cobalt catalyst "8" were also investigated over a temperature range of 190 - 230°C.

RESULTS

The following tables I - V list the data of fourteen typical runs. The temperatures of the line, furnace and reaction chamber are noted, together with the weight of catalyst.

In columns one and two the time and pressure readings on manometer M are presented. In columns three and four, the rate of change of pressure at various times are tabulated.

In this first series of runs using Catalyst "C", air was admitted to the reaction chamber after activation, thus oxidizing the reduced catalyst. Here the pressure decreases with time. It would seem to indicate that by allowing air to enter, the catalyst was poisoned and the overall result was one of adsorption rather than decomposition.

On analysing the products, it was found that only methyl alcohol was present.

MeOH over Catalyst "C" at 200°C

Wt. of sample = 30 gms.

Temp. line = 104°C

Temp. Furnace = 110°C

Temp. of Reaction Chamber = 200°C

TABLE I

Time - seconds	Press. cms. Hg	Time - seconds	dP/dT
0	22.8	20	-.0334
2	22.3	40	-.0186
6	21.8	60	-.0138
17	21.3		
42	20.8	120	-.00910
76	20.3	180	-.00595
130	19.8	280	-.00460
210	19.3		
317	18.8		
405	18.5		
466	18.3		

MeOH over Catalyst "C" at 210°C

Temp. line = 97°C

Temp. Furnace = 110°C

Temp. of Reaction Chamber = 210°C

TABLE II

Time - seconds	Press. cms. Hg	Time - seconds	dp/dT
0	19.7	10	-.236
4	15.7	20	-.0735
10	13.7	40	-.0297
16	12.7	60	-.0171
21	12.2	80	-.0091
30	11.7	100	-.0052
50	11.2	120	-.003
90	10.7	140	-.0025
115	10.5	180	-.00072

Methyl Alcohol over Catalyst "C" at 200°C

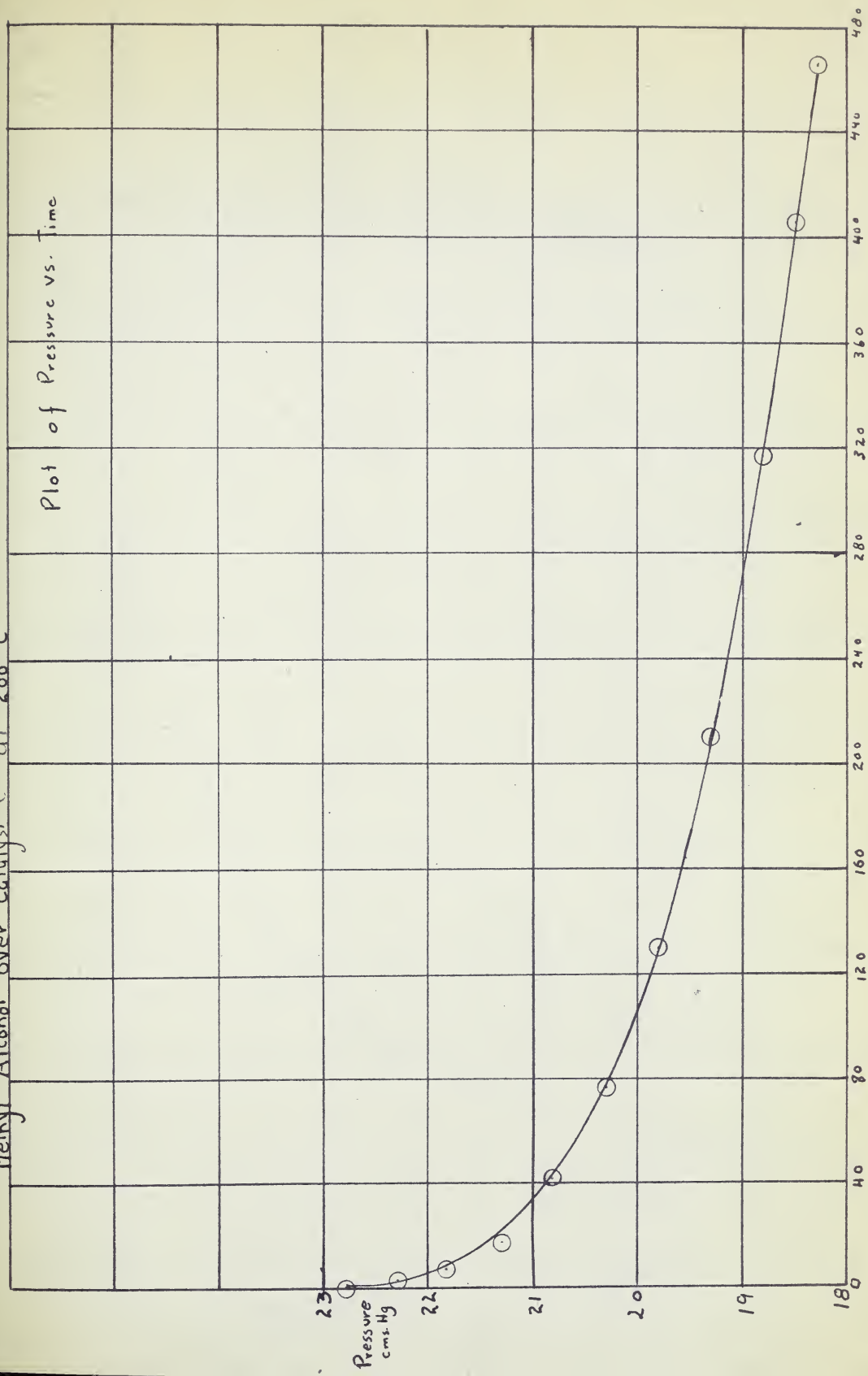


Fig. 6 Time - Seconds

Plot of $\frac{dP}{dt}$ vs Time using CH_3OH at 200°C over Catalyst "C"

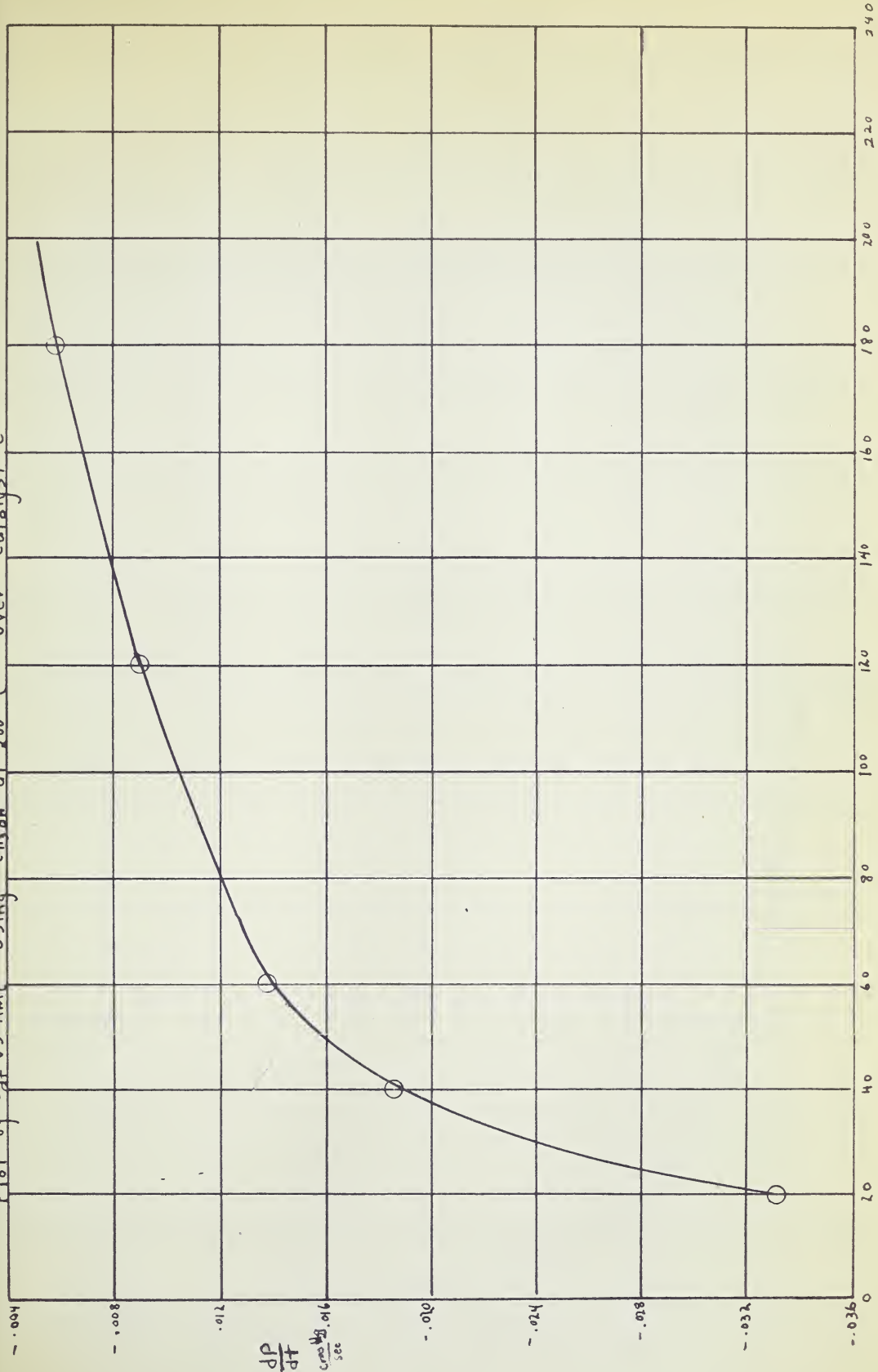


Fig. 7 Time - Seconds

Methyl Alcohol at 210°C over Catalyst C

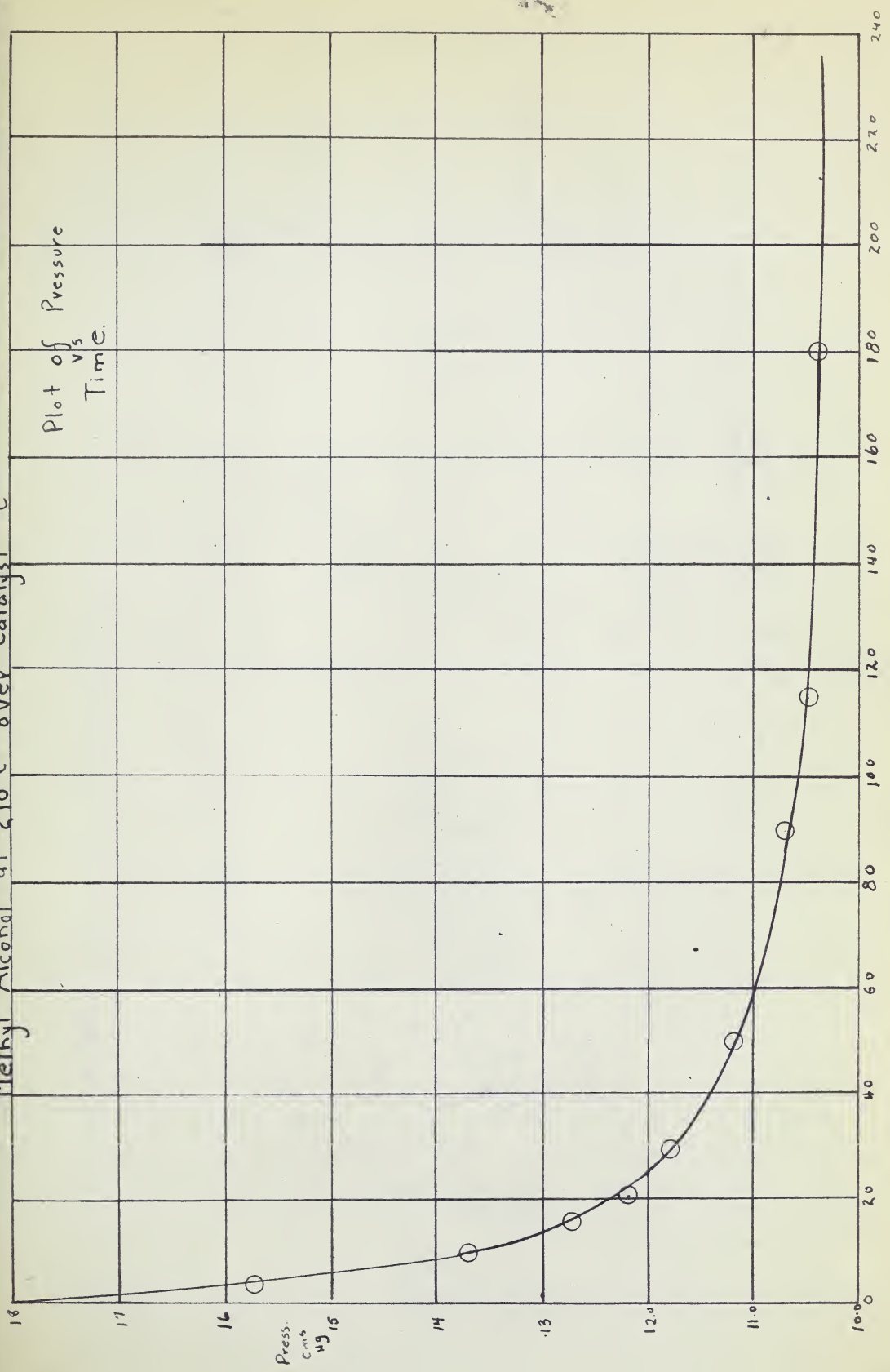


Fig. 8 Time - Seconds

CH₃OH at 210°C over Catalyst "C"

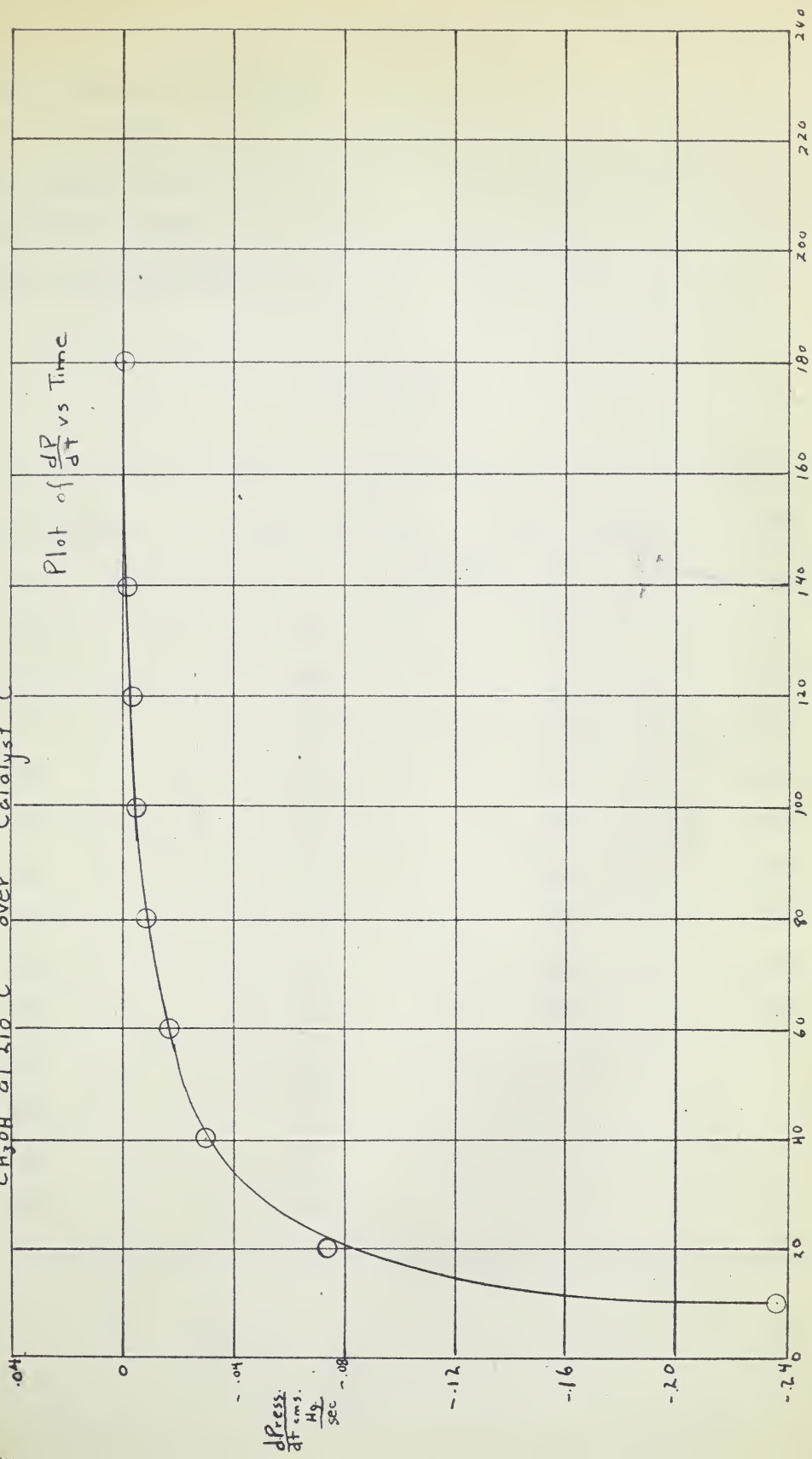


Fig. 9. Time - Seconds

EtOH over Catalyst "C" at 200°C

Temp. line = 109°C

Temp. Furnace = 119°C

Temp. Reactor = 200°C

Pressure = 54.8 cms. Hg

TABLE III

Time - seconds	Press. cms. Hg	Time - seconds	dP/dT
0	21.8	10	-.208
4	20.8	20	-.055
7	19.8	40	-.027
12	18.8	60	-.017
16	18.3	80	-.013
23	17.8	100	-.0099
35	17.3	120	-.0076
56	16.8	160	-.0053
82	16.5	180	-.0050
102	16.3		
122	16.1		
183	15.8		
240	15.5		

ETOH over Catalyst "C" at 210°C

Temp. line = 105°C

Temp. Furnace = 111°C

Temp. Reactor = 210°C

Press. = 56.2 cms. Hg

TABLE IV

Time - seconds	Press. cms. Hg	Time - seconds	dP/dT
0	26.2	10	.172
2	25.2	20	.097
6	24.2	40	.037
11	23.2		
14	22.7	60	.0225
26	21.7		
32	21.2	80	.0146
48	20.7		
72	20.2	100	.0120
91	19.9		
105	19.7	120	.0096
180	19.2		
240	18.8	160	.0063
		180	.0063

Ethyl Alcohol at 200°C over Catalyst "C"

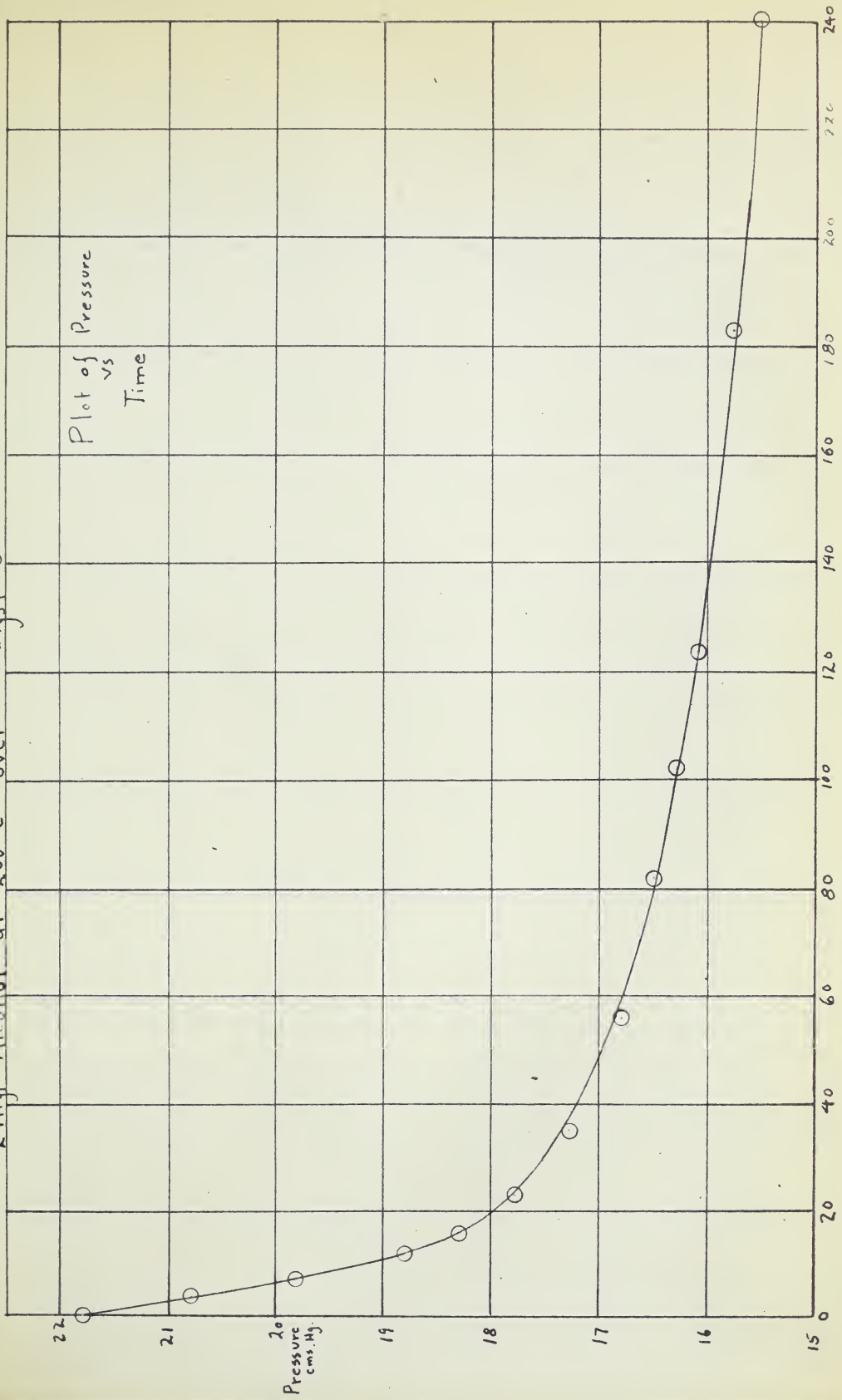


Fig. 10 Time - Seconds

Plot of $\frac{dp}{dt}$ vs Time using CH_3COOH at 20°C

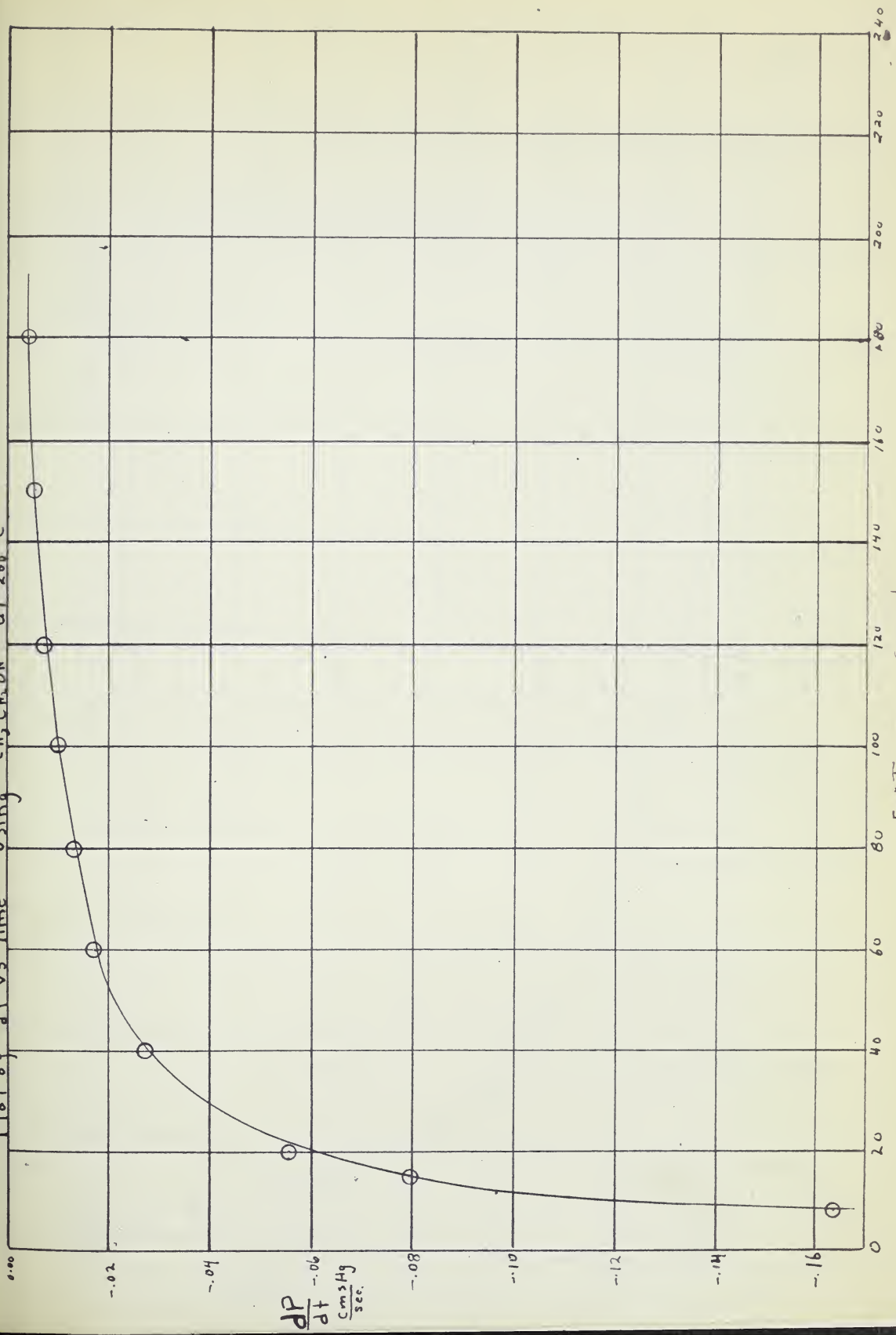


Fig. Time - Seconds

Carbazole at 210°

Plot of Pressure
vs
Time

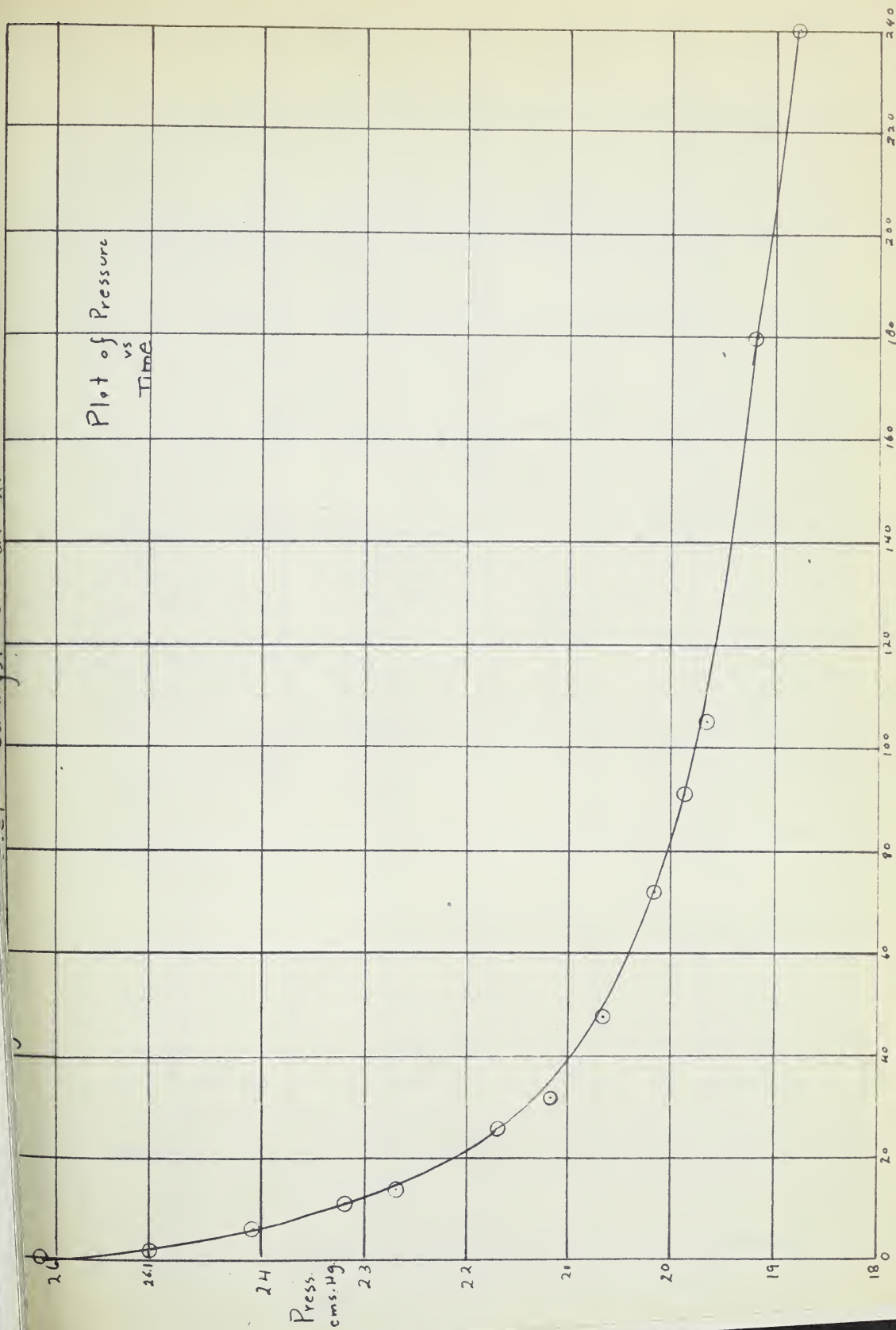


Fig. 12 Time - Seconds

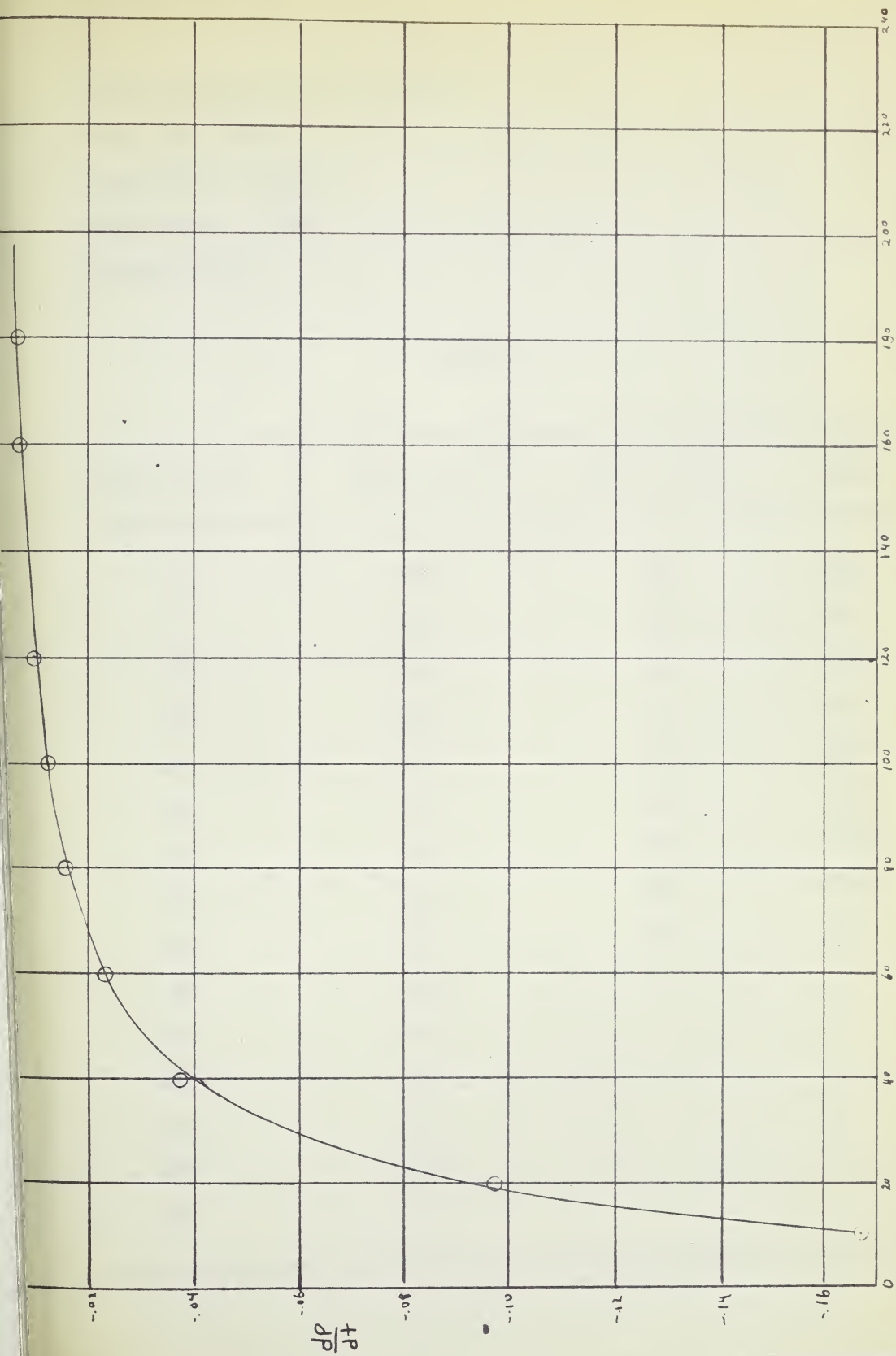


Fig. 13 Time - Seconds

Acetone over Catalyst "C" at 200°C

Temp. line = 100°C

Temp. Furnace = 108°C

Temp. Reactor = 200°C

Pressure = 55.7

TABLE V

Time - seconds	Press. cms. Hg	Time - seconds	dP/dT
0	35.7	10	.188
4	34.2	20	.067
8	33.2	40	.034
10	32.7	60	.026
16	31.7	80	.021
18	31.2	100	.0174
25	30.7	120	.0173
31	30.2	160	.0103
45	29.7	180	.01
58	29.2		
78	28.7		
104	28.2		
135	27.7		
180	27.2		
237	26.7		

Acetone over Catalyst C at 200°C

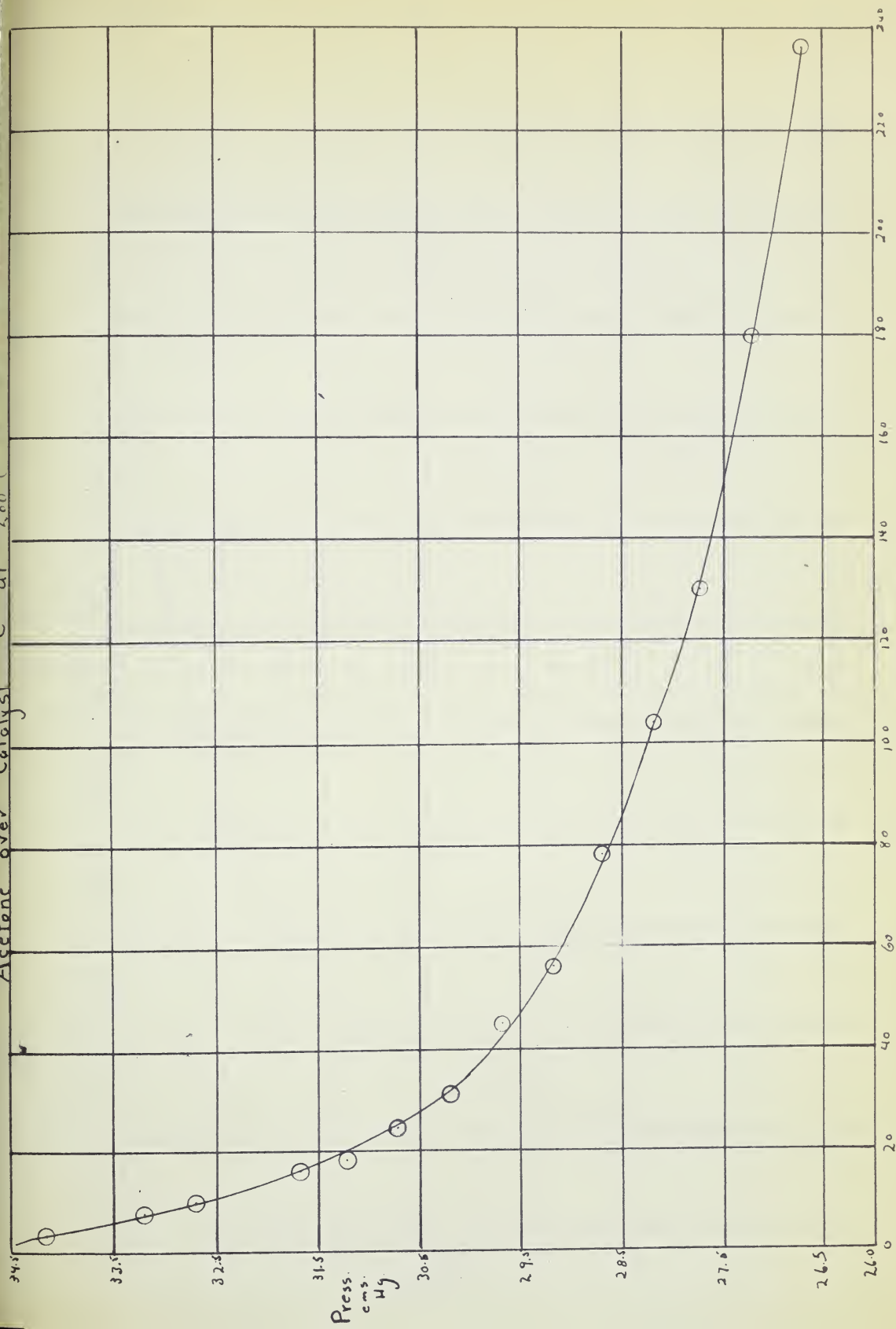


Fig 124 Time - Seconds

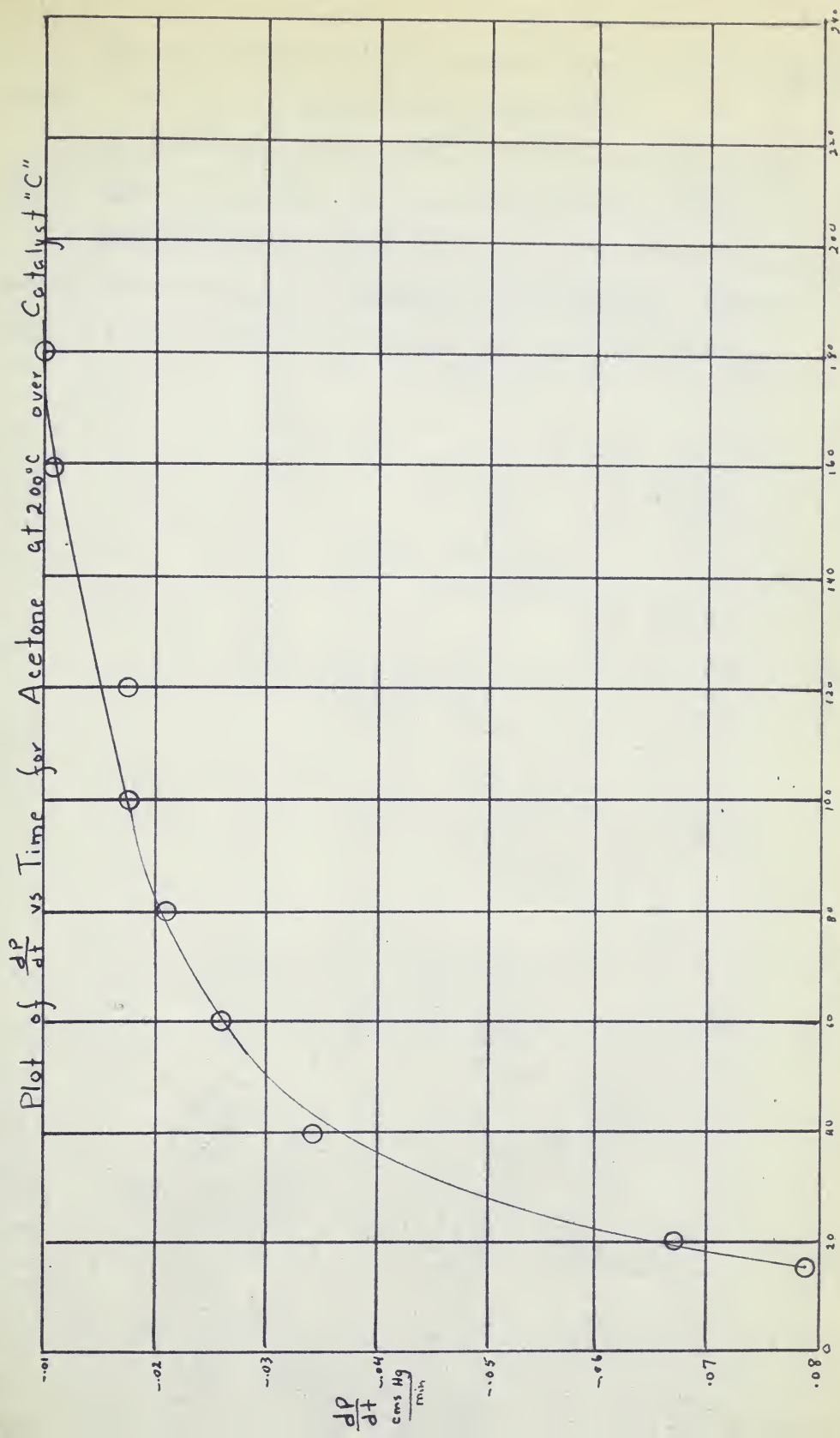


Fig. 15 Time - Minutes

Table VI compares the rates of pressure change " dp/dt " at various times " t " with various reactants at two temperatures.

It appears that over the oxidized catalyst no decomposition is taking place. Instead we may have an adsorption with the rate depending on diffusion.

These results may have some importance in considering the decrease in catalytic activity as the synthesis reaction proceeds. This decrease in activity makes it necessary to reactivate the catalyst frequently.

TABLE VI

COMPARISON OF RATES OF ADSORPTION

Methanol 200°C			Methanol 210°C			Ethanol 200°C			Ethanol 210°C			Acetone 200°C		
dP/dT			dP/dT			dP/dT			dP/dT			dP/dT		
Time	Run	Run	Run	Run	Run	Run	Run	Run	Run	Run	Run	Run	Run	Run
sec.	# 4	# 5	# 1	# 2	# 2	# 1	# 2	# 3	# 1	# 2	# 1	# 2	# 3	# 4
10			.14	.14	.2	.2	.2		.17	.17	.100	.188	.105	.074
20	.034	.033	.065	.061	.070	.070	.052		.10	.10	.059	.0675	.0475	.0465
40	.021	.0186	.026	.025	.025	.025	.026		.037	.035	.029	.0348	.0290	.026
60	.015	.0138	.016	.016	.014	.014	.017		.025	.022	.0229	.0255	.0225	.020
80	.012	.0116	.011	.011	.010	.010	.013		.016	.016	.0020	.0210	.0200	.017
100	.010	.010	.007	.007	.0088	.0088	.0095		.012	.012	.020	.0180	.0178	.0157
120	.0088	.0088	.005	.005	.0077	.0077	.008		.0099	.010	.0121	.0173	.0130	.0132
140	.0079	.0079	.004	.004	.0053	.0053	.0062		.0080	.0090	.0089	.0125	.0110	.0118
160	.0070	.0077	.003	.003	.005	.005	.0055		.007	.008	.007	.0105	.0095	.0105
180	.0064	.0064	.002	.002	.005	.005	.005		.006	.008	.006	.0100	.0083	.009

Values for dP/dT are negative.

Tables VII to XXXVI list the data of typical runs for the decomposition of methyl alcohol, ethyl alcohol, and formic acid, and the synthesis from $\text{CO} + 2\text{H}_2$. The catalyst used here was $\text{Co} : \text{ThO}_2 : \text{MgO} : \text{Kieselguhr}$, 100 : 6 : 12 : 200 : (Catalyst "8"). The catalyst was reduced and activated with special precautions to prevent air from coming in contact with it. It was assumed that the catalyst surface in these decompositions was similar to the catalyst surface in the synthesis of hydrocarbons. The temperature used (185 - 230°C) is the range used in the synthesis of hydrocarbons.

For each run listed here there are two tables presented. These runs are included as typical of the results at the various temperatures and with the various reactors. The first table of each set represented by Tables VII, IX, XI, etc. show the pressure change vs. time. Tables VIII, X, XII, etc. show in column one - time in minutes; column two - apparent pressure in cms. Hg; and in column three - correction "x" which must be subtracted from column two to obtain the actual pressure, according to the method indicated in Fig. 4. Column four shows P_c , the corrected pressure difference. Column five gives the corrected final pressure P_f , minus the corrected pressure P_c . Column six shows the log of $P_f - P_c$.

Fig. 16 shows a typical decomposition curve of Pressure vs. Time. Fig. 17 shows the plot of $\log P_f - P_c$ vs. Time for the rate of decomposition. This plot gives a straight line showing that the decomposition follows a first order rate equation.

The other figures list similar data to these.

DECOMPOSITION OF METHANOL OVER CATALYST # 8

AT 190°C

Weight of Catalyst = 30 gms.

Temp. line = 92°C

Temp. Furnace = 111°C

Temp. Reaction Vessel = 190°C

Pressure = 56.9 cms. Hg

TABLE VII

Time - min.		Pressure (Act) cms. Hg	Press. rdgs.
min.	sec.		
0	0	17.9	39.0
2	19	18.9	38.0
5	20	20.9	36.0
7	56	22.9	34.0
10	26	24.9	32.0
12	40	26.9	30.0
18	33	31.9	25
20	26	32.9	24
26	03	34.9	22
35	12	36.9	20
42	26	37.9	10

TABLE VIII

Time - minutes	Press. cms.=P	Correction x	$P_c = P - x$	$P_f - P_c$	$\log P_f - P_c$
0	17.9	0	17.9	17.6	1.25
10	24.5	.5	24.0	9.5	.98
20	32.4	1.1	31.3	4.2	.62
30	35.9	1.8	34.1	1.4	.15
40	37.5	2.4	35.1	.4	-.40
50	38.4	2.9	35.5		
56	38.8	3.3	35.5		

Methyl Alcohol over Catalyst "8" at 190°C

Plot of Pressure
vs
Time

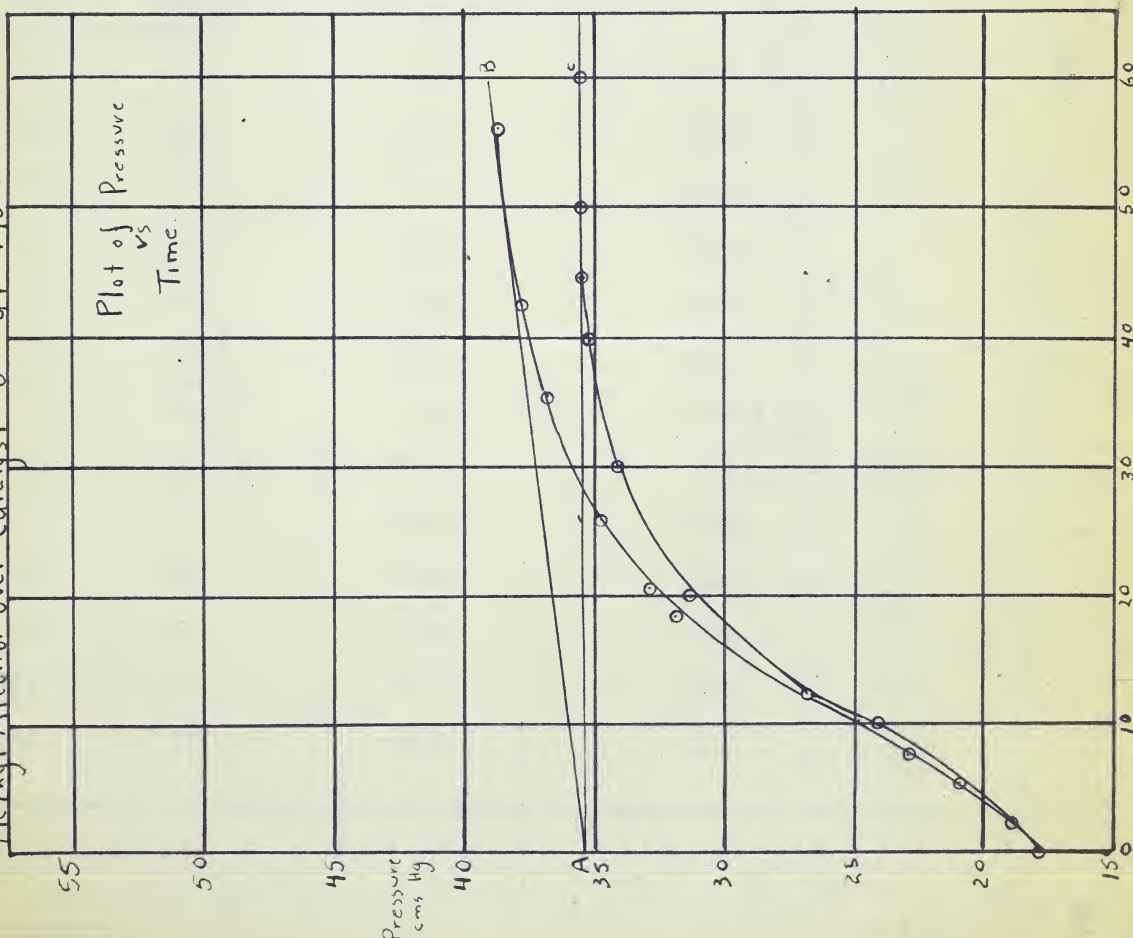


Fig. 16 Time - Minutes.

Plot of $\log P_0/P_t$ vs Time for CH_3OH

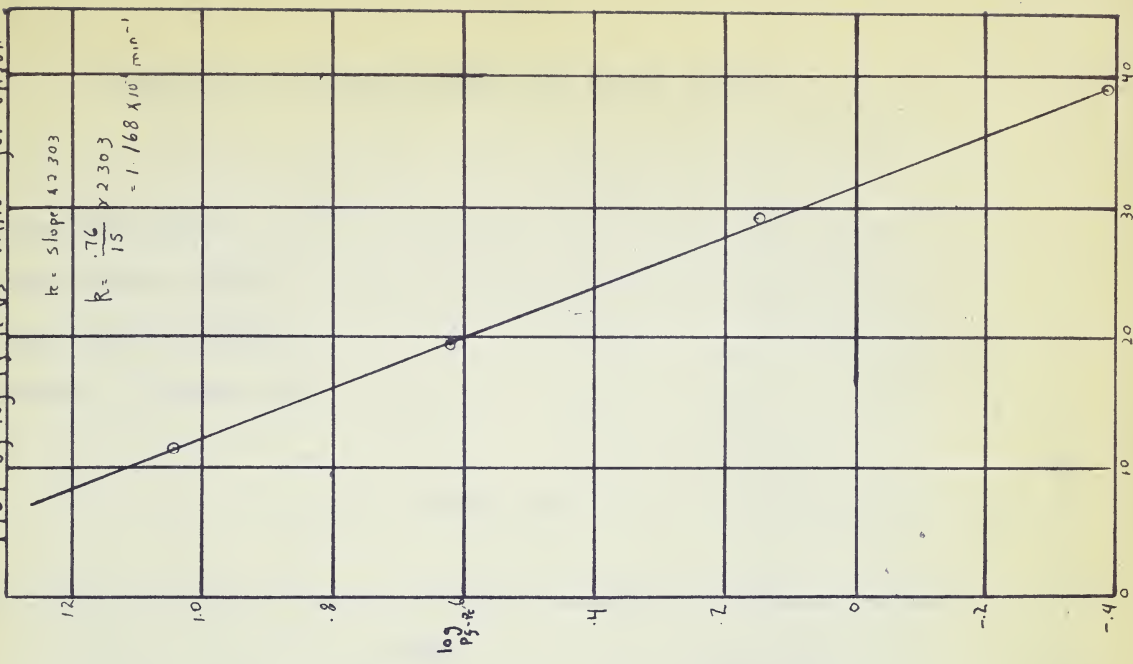


Fig. 17. Time - Minutes

DECOMPOSITION OF METHANOL OVER CAT. #8 AT 200°C

Temp. Line = 97°C

Temp. Furnace = 103°C

Temp. Reactor = 210°C

Pressure = 56.9 cms. Hg

TABLE IX

Time		Press.	Press. Corr.
Min.	Sec.		
0	0	35.0	21.9
0	34	34.0	22.9
1	15	32.0	24.9
1	40	30.0	26.9
2	20	28.0	28.9
3	13	26.0	30.9
4	25	24.0	32.9
5	55	22.0	34.9
8	30	20.0	36.9
12	19	18.0	38.9
16	41	17.0	39.9
22	24	16.0	40.9
34	17	15.1	41.8

TABLE X

$$P_f = 37.0$$

Time - minutes	Press.	Corr. "x"	$P_c = P - x$	$P_f - P_c$	$\log P_f - P_c$
0	21.9		21.9	15.1	1.18
2.5	29.0	.5	28.5	8.5	.93
5.0	33.8	.9	32.9	4.1	.61
7.5	36.0	1.4	34.6	2.4	.38
10.0	37.8	1.7	36.1	.9	-.046
12.5	39.0	2.2	36.8	.2	-.70
15.0	39.5	2.5	37.0		
17.5	40.0	3.0	37.0		
20.0	40.4	3.4	37.0		
22.5	40.8	3.8	37.0		

Methyl Alcohol over Catalyst "B" at 210°C

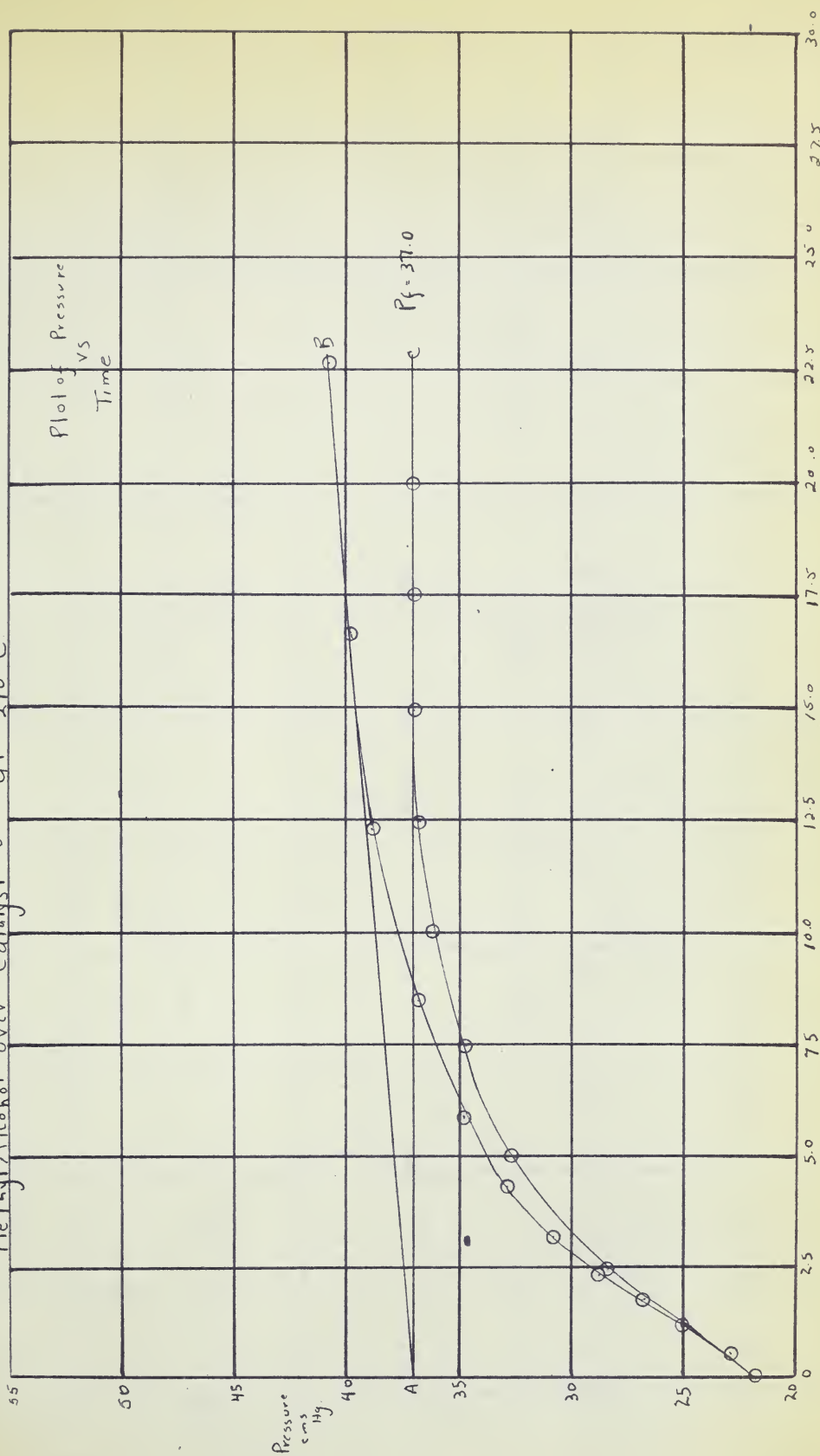


Fig. 18 Time - Minutes

Plot of $\log_0 P_t - P_\infty$ vs Time using CH_3OH at 210°C

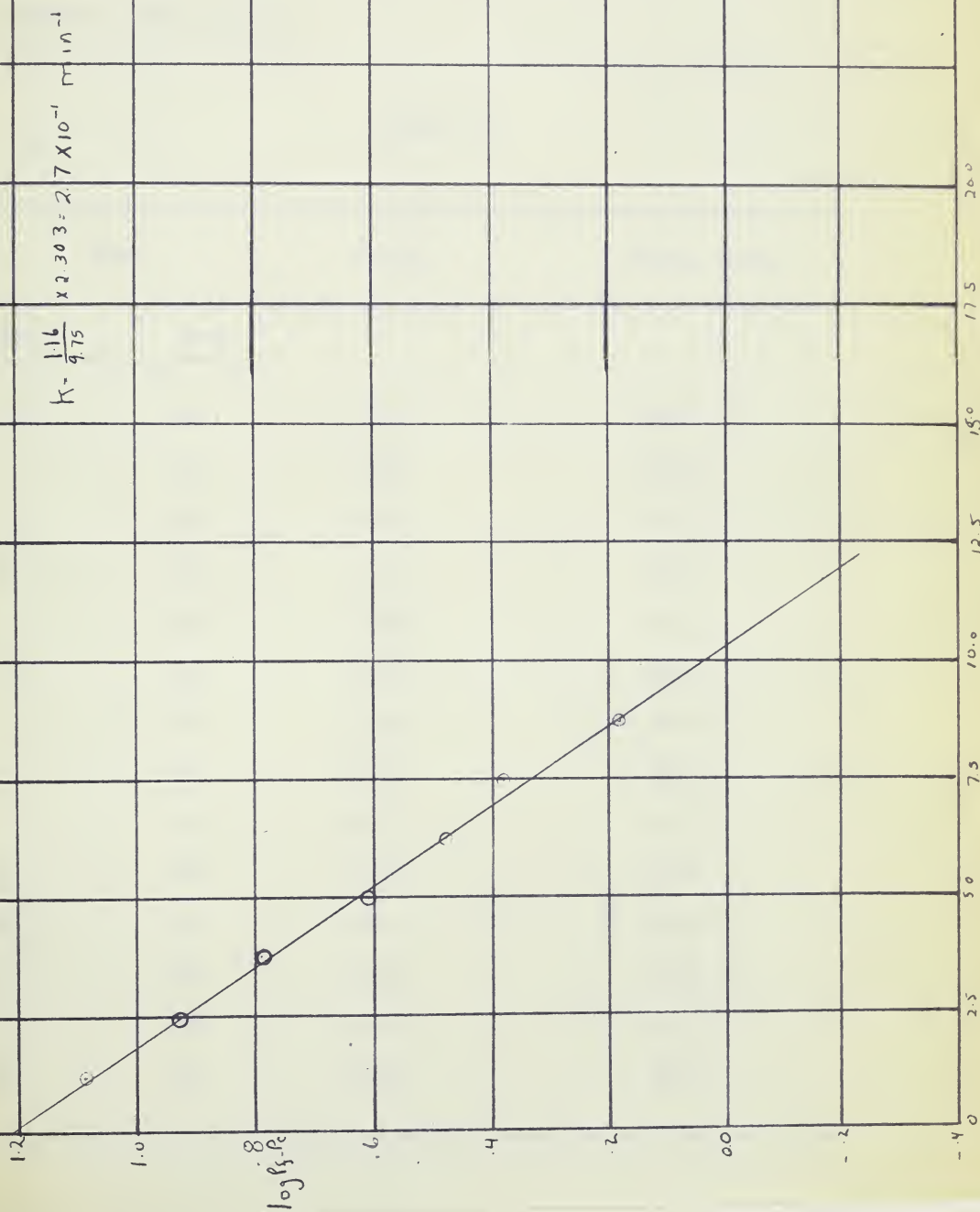


Fig 19 Time - Minutes

DECOMPOSITION OF METHANOL OVER CAT. #8 AT 200°C

Temp. Line = 97°C

Temp. Furnace = 110°C

Temp. Reactor = 200°C

Pressure = 56.5 cms. Hg

TABLE XI

Time		Press.	Press. Corr.
Min.	Sec.		
0	00	36.5	20.0
	08	36.0	20.5
	35	35.0	21.5
1	01	34.0	22.5
1	45	32.0	24.5
2	41	30.0	26.5
3	20	28.0	28.5
4	26	26.0	30.5
6	11	24.0	32.5
8	50	22.0	34.5
12	39	20.0	36.5
15	33	19.0	37.5
19	25	18.0	38.5
28	56	17.0	39.5

TABLE XII

$P_f = 37.5$					
Time	Press.	x	$P - x$	$P_f - P_c$	$\log P_f - P_c$
0	20.0	0	20.0	17.5	1.24
2.5	26.0	.1	25.9	11.6	1.06
5.0	31.2	.2	31.0	6.5	.82
7.5	33.8	.4	33.4	4.1	.61
10.0	35.3	.5	34.8	2.7	.43
12.5	36.5	.6	35.9	1.6	.20
15.0	37.4	.8	36.6	.9	-.046
17.5	38.0	1.0	37.0	.5	-.30
20.0	38.5	1.1	37.4	.1	-1.0
22.5	38.7	1.2	37.5		
25.0	38.9	1.4	37.5		
27.5	39.0	1.5	37.5		
30.0					

Methyl Alcohol over Catalyst "8" at 200°C

Plot of Pressure
vs
Time.

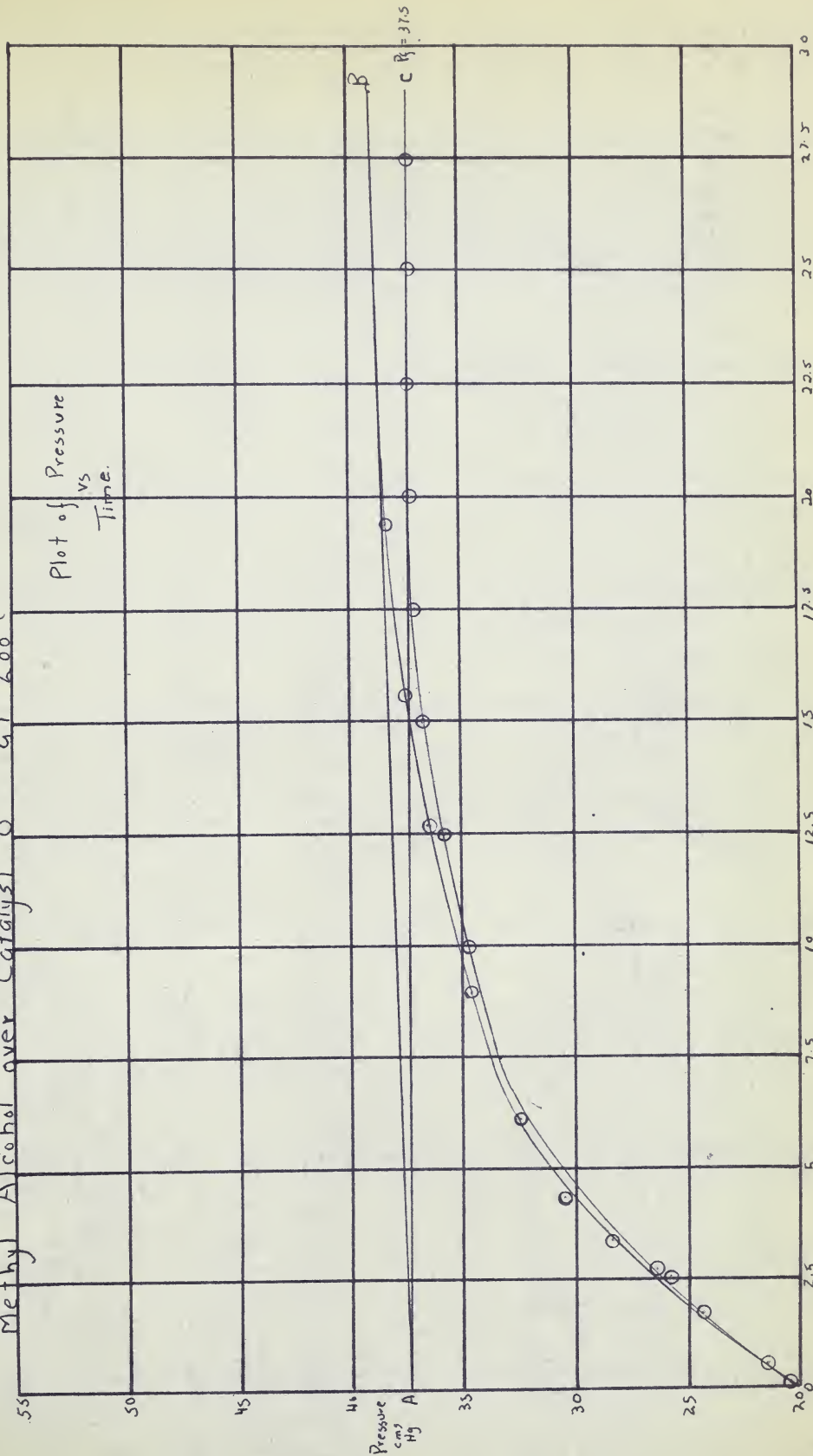


Fig. 20 Time - Minutes

Plot of $\log P_0 - P_t$ using CH_2OH at 20.0°C .

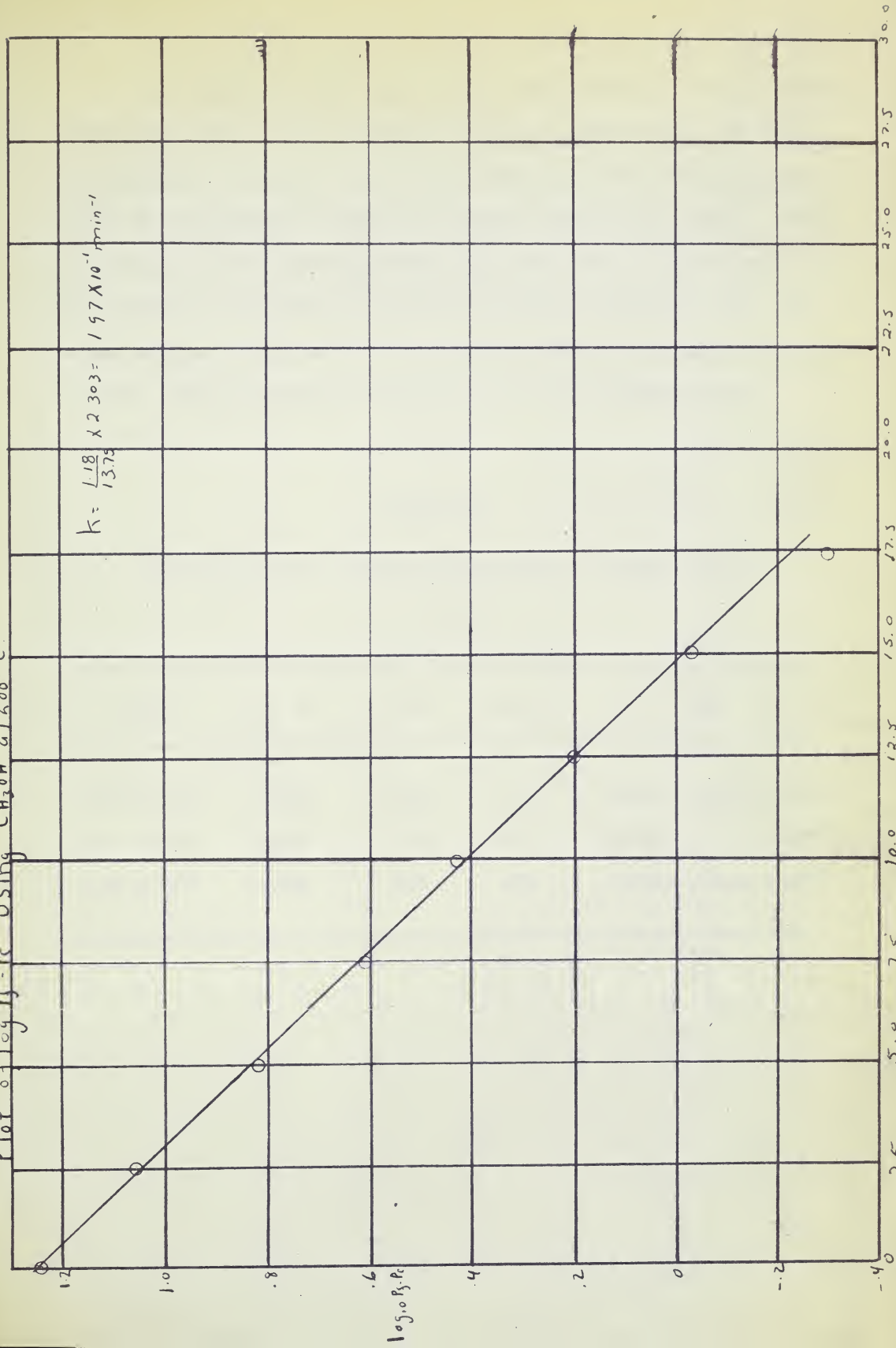


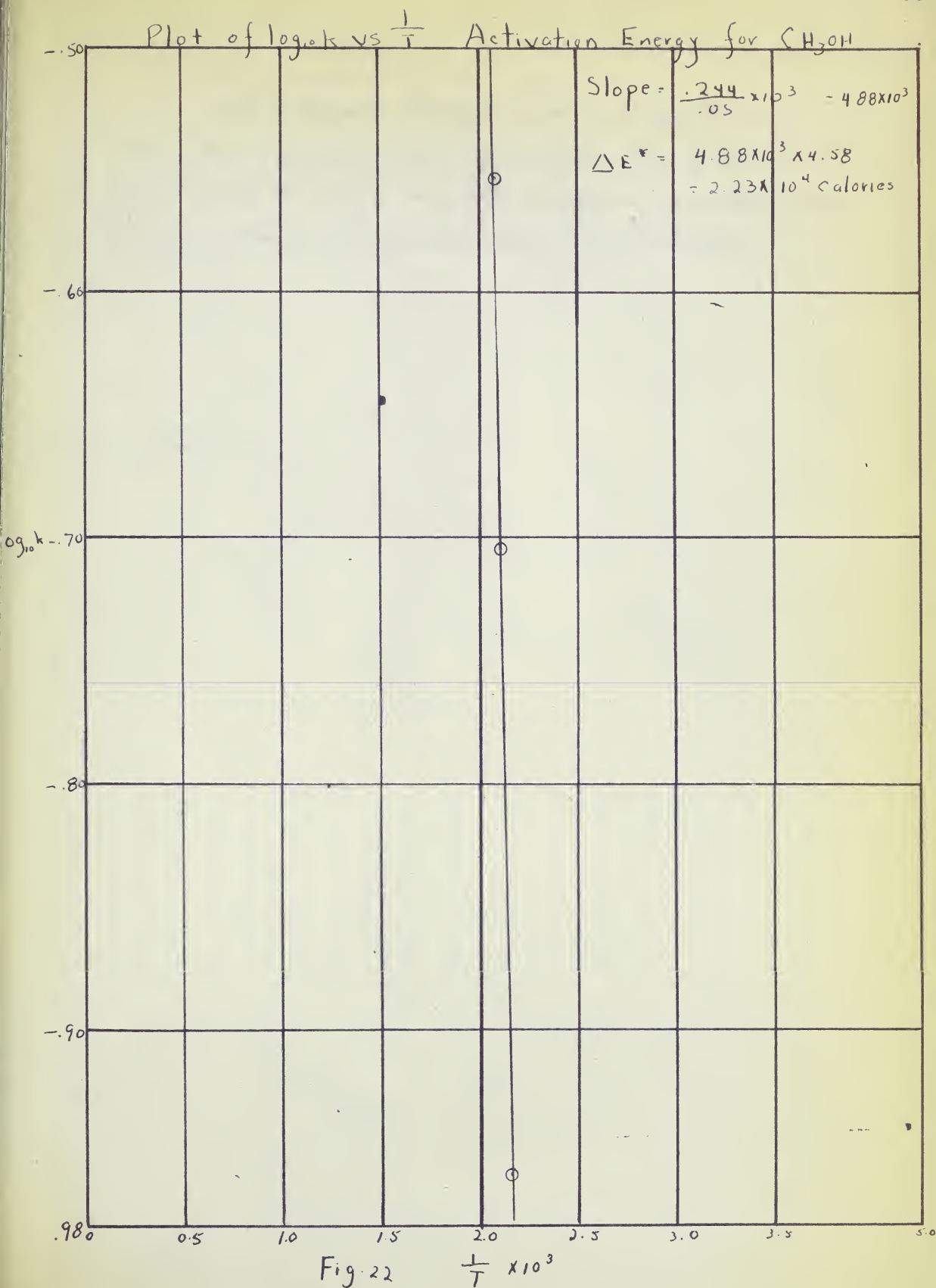
Fig. 21 Time - Minutes

Table XIII lists the data for the decomposition of methyl alcohol. Column one shows k - the velocity constant as obtained from the slopes of the graphs of $\log P_f - P_c$ vs Time. Column two shows $\log k$; column three the temperature at which the velocity constant was found. Column four lists the absolute temperature and column five - the reciprocal of the absolute temperature. Fig. 22 is the plot of $\log k$ vs. $1/T$. The slope obtained multiplied by 4.58 gives the activation energy for methyl alcohol. This activation energy was found to be 22,300 calories.

TABLE XIII

Activation Energy For The Decomposition of Methyl Alcohol

$k, \text{ min}^{-1}$	$\log k$	$t^\circ\text{C}$	$T^\circ\text{A}$	$1/T$
1.10×10^{-1}	-.959	190	463	.00216 = 2.16×10^{-3}
2.8×10^{-1}	-.553	210	483	.00207 = 2.07×10^{-3}
1.97×10^{-1}	-.704	200	473	.002114 = 2.11×10^{-3}



Figures 23 to 28 give similar results to those of methyl alcohol for the decomposition of ethyl alcohol. Table XX gives the data necessary for finding the activation energy for the decomposition of ethyl alcohol. This activation energy is 28,000 calories.

DECOMPOSITION OF ETHANOL OVER CAT. #8 AT 200°C

Wt. of catalyst = 30 gms.

Temp. Line = 104°C

Temp. Furnace = 125°C

Temp. Reactor = 200°C

Pressure = 56.2 cms. Hg

TABLE XIV

Time		Press. cms. Hg	Press. Rdg
<u>Min.</u>	<u>Sec.</u>		
0	0	36.5	19.7
	30	36.5	19.7
	58	36.0	20.2
3	10	35.0	21.2
6	10	34.0	22.2
15	42	33.0	23.2
24	51	32.0	24.2
32	00	31.0	25.2

TABLE XV

$$P_f = 23.10$$

Time - Min.	Press. cms. Hg	Correc. "x"	P - x	$P_f - P_c$	$\log P_f - P_c$
0					
2.5	21.1	.08	20.92	2.08	.32
5.0	21.91	.12	21.79	1.31	.12
7.5	22.32	.20	22.12	.98	-.01
10.0	22.61	.30	22.31	.79	-.10
12.5	22.89	.39	22.50	.60	-.23
15.0	23.11	.45	22.66	.44	-.36
17.5	23.33	.51	22.82	.28	-.55
20.0	23.53	.60	22.93	.17	-.77
22.5	23.70	.69	23.01	.09	-1.05
25.0	23.80	.75	23.05	.05	-1.30
27.5	23.90	.80	23.10		
30.0	24.00	.90	23.10		

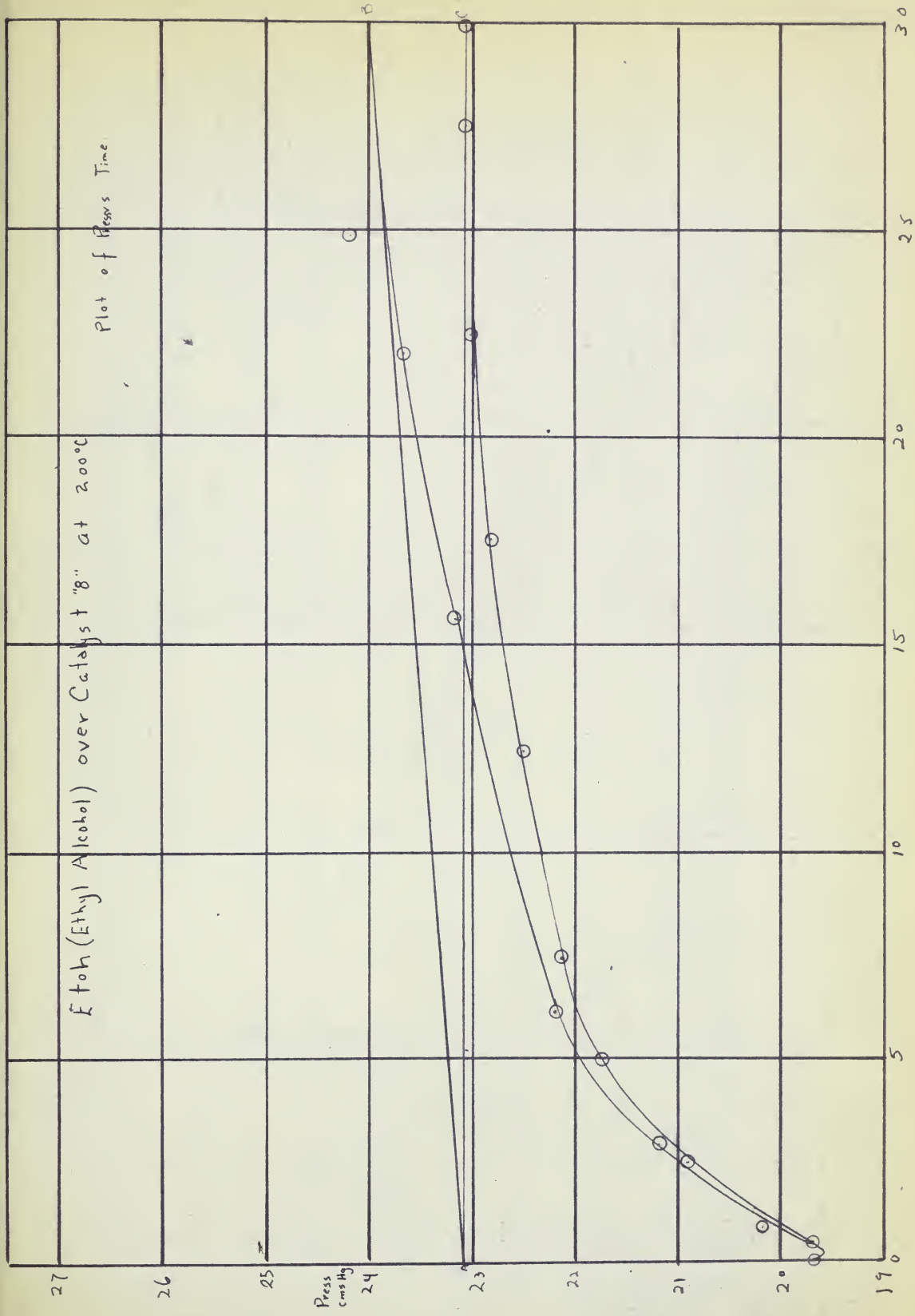


Fig 23 Time - Minutes

Plot of $\log_{10} P_f - P_c$ using $\text{CH}_3\text{CH}_2\text{OH}$ at 20.0°C

$$k = \frac{.96}{20.5} \times 2.303 = 1.08 \times 10^{-1} \text{ min}^{-1}$$

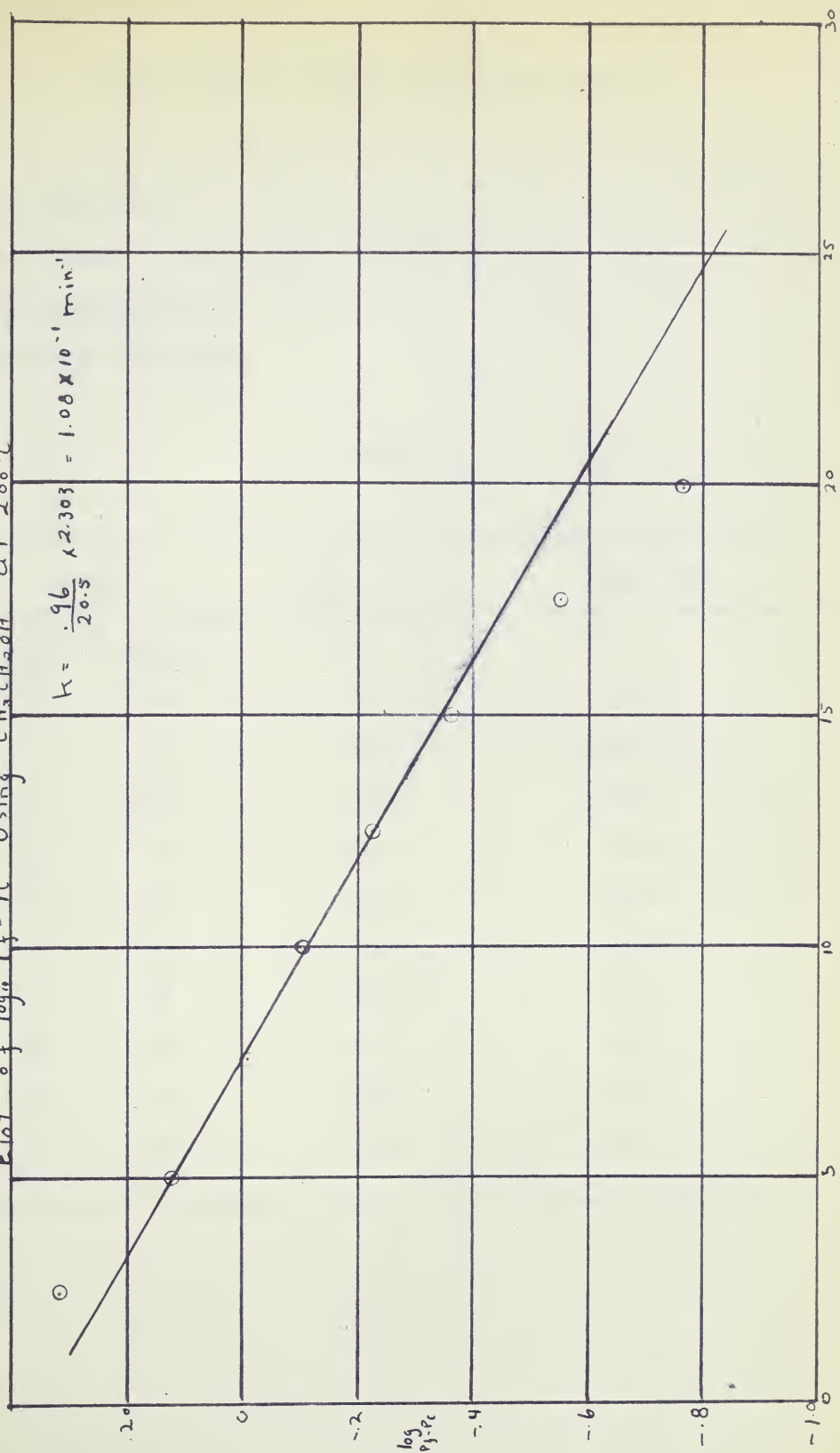


Fig. 24 Time - Minutes

DECOMPOSITION OF ETHANOL OVER CAT. #8 AT 210°C

Temp. Line = 94°C

Temp. Furnace = 110°C

Temp. Reactor = 210°C

Pressure = 56.3 cms. Hg

TABLE XVI

Time		Press. cms. Hg	Press. Rdg
<u>Min.</u>	<u>Sec.</u>		
0	00	36.0	20.3
	30	36.9	19.4
1	00	36.5	19.8
3	14	36.0	20.3
4	06	35.5	20.8
6	05	35.0	21.3
9	00	34.5	21.8
10	30	34.0	22.3
26	30	33.6	22.7
39	05	33.5	22.8

TABLE XVII

 $P_f = 22.50$ cms. Hg

Time - min.	Press. cms. Hg	Correction "x"	P - x	$P_f - P_c$	$\log P_f - P_c$
2.5	19.75	0	19.75	2.75	.44
5.0	21.00	.03	20.97	1.53	.18
7.5	21.50	.04	21.46	1.04	.02
10.0	21.91	.10	21.81	.69	-.16
12.5	22.20	.11	22.09	.41	-.38
15.0	22.39	.12	22.27	.23	-.64
17.5	22.49	.15	22.34	.16	-.80
20.0	22.55	.19	22.36	.14	-.85
22.5	22.60	.20	22.40	.10	-1.00
25.0	22.65	.21	22.44	.06	-1.22
27.5	22.70	.22	22.48	.02	
30.0	22.72	.22	22.50		

Ethyl Alcohol over Catalyst "g" at 210°C

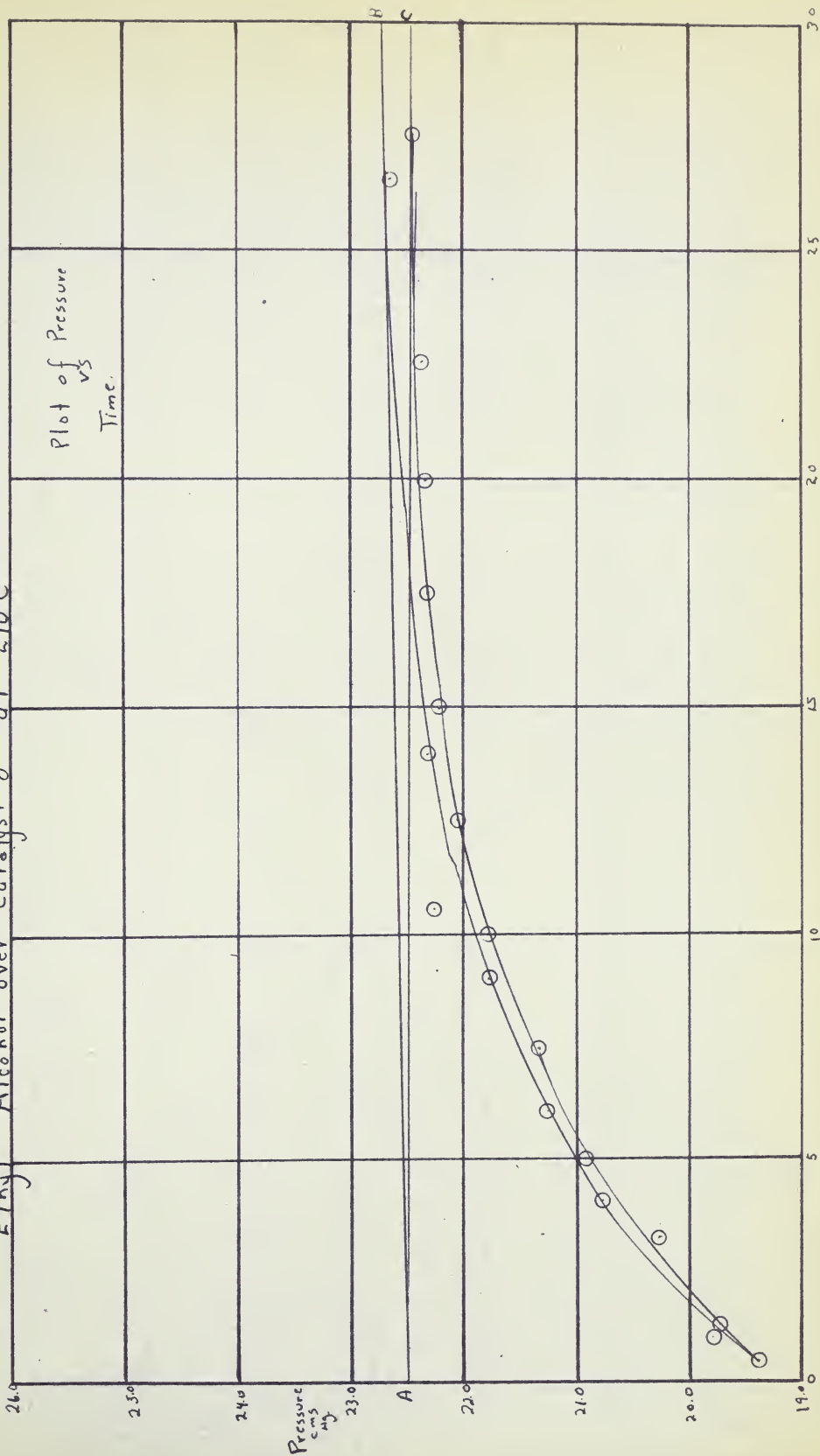


Fig. 25. Time - Minutes

pg. 22.5

Plot of $\log_{10} p_3 - p_1$ vs time using CH_3COOH at 210°C .

$$k = \frac{13.4}{16.25} \times 2.303 = 1.9 \times 10^{-1} \text{ min}^{-1}$$

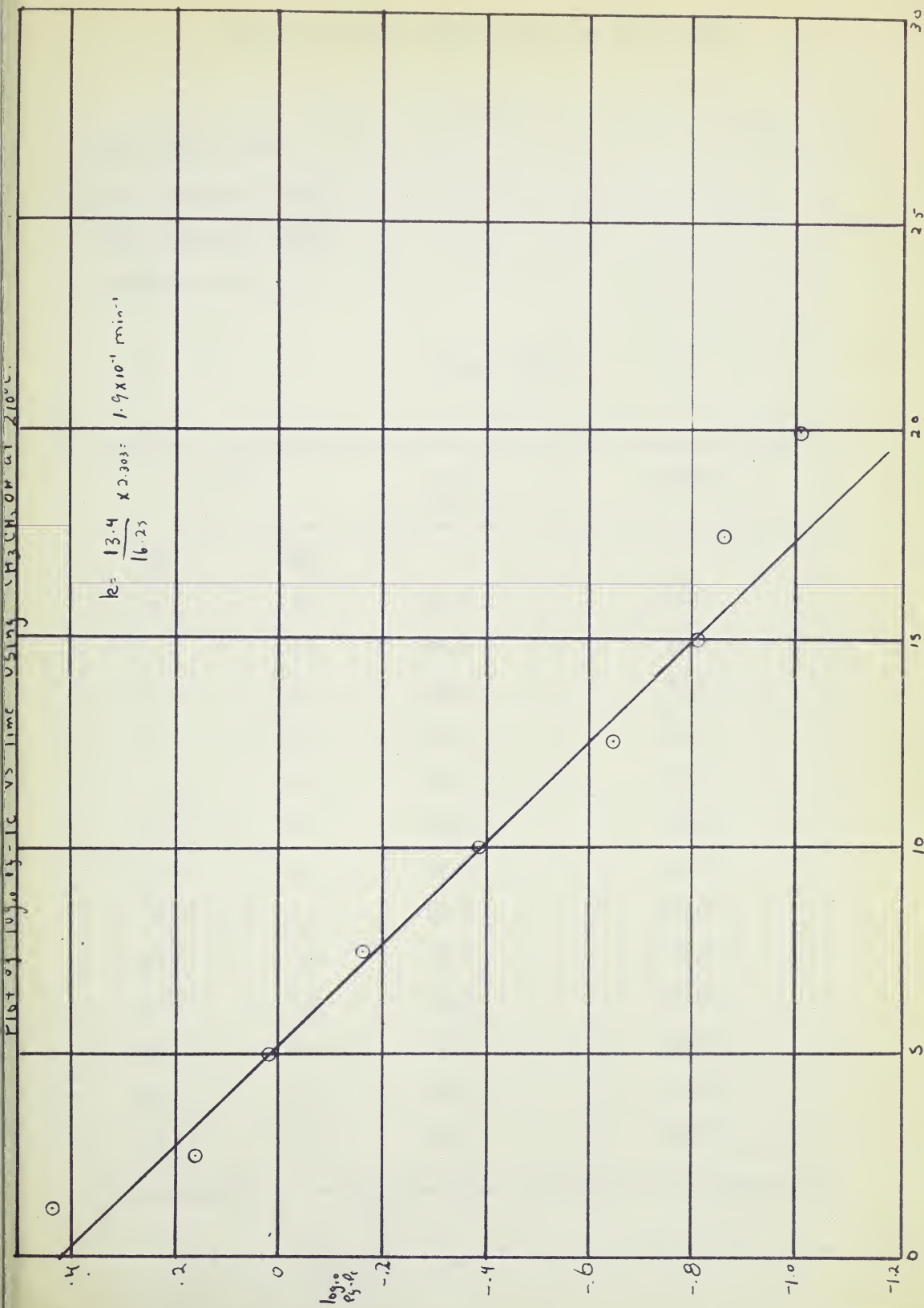


Fig. 26 Time - Minutes



DECOMPOSITION OF ETHANOL OVER CAT. #8 AT 220°C

Temp. Line = 92°C

Temp. Furnace = 105°C

Temp. Reactor = 220°C

Pressure = 55.7

TABLE XVIII

Time		Press. cms. Hg	Press.
<u>Min.</u>	<u>Sec.</u>		
0	00	33.0	22.7
	26	32.5	23.2
1	05	32.0	23.7
2	30	31.0	24.7
4	02	30.0	25.7
5	30	29.5	26.2
6	54	29.0	26.7
8	45	28.5	27.2
10	40	28.0	27.7
11	45	27.5	28.2
17	10	27.0	28.7
23	20	26.5	29.2
41	55	26.1	29.6

TABLE XIX

$$P_f = 28.9$$

Time - min.	Press. Cms. Hg	Correct. x	P - x	$P_f - P_c$	$\log P_f - P_c$
0	22.70	0	22.70	6.20	.79
2.5	24.75	.05	24.70	4.20	.62
5.0	26.10	.10	26.00	2.90	.46
7.5	26.83	.15	26.68	2.22	.35
10.0	27.50	.19	27.31	1.59	.20
12.5	28.05	.24	27.81	1.09	.03
15.0	28.50	.30	28.20	.70	-.15
17.5	28.82	.36	28.46	.44	-.36
20.0	29.10	.40	28.70	.20	-.70
22.5	29.27	.46	28.81	.09	-1.05
25.0	29.37	.50	28.87	.03	-1.52
27.5	29.45	.50	28.90		

Ethyl Alcohol over Catalyst "8" at 220°C

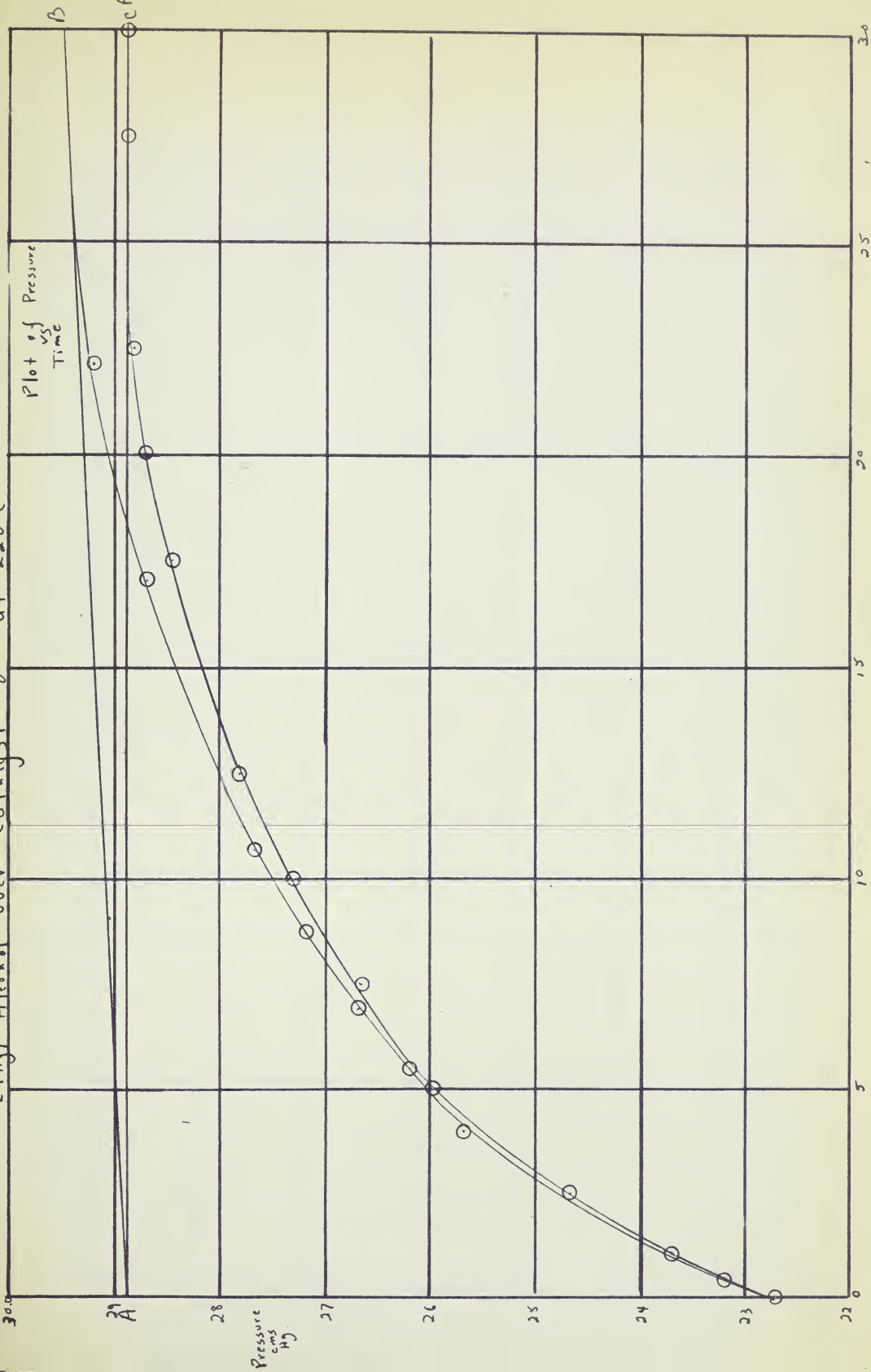


Fig. 27 Time - Minutes

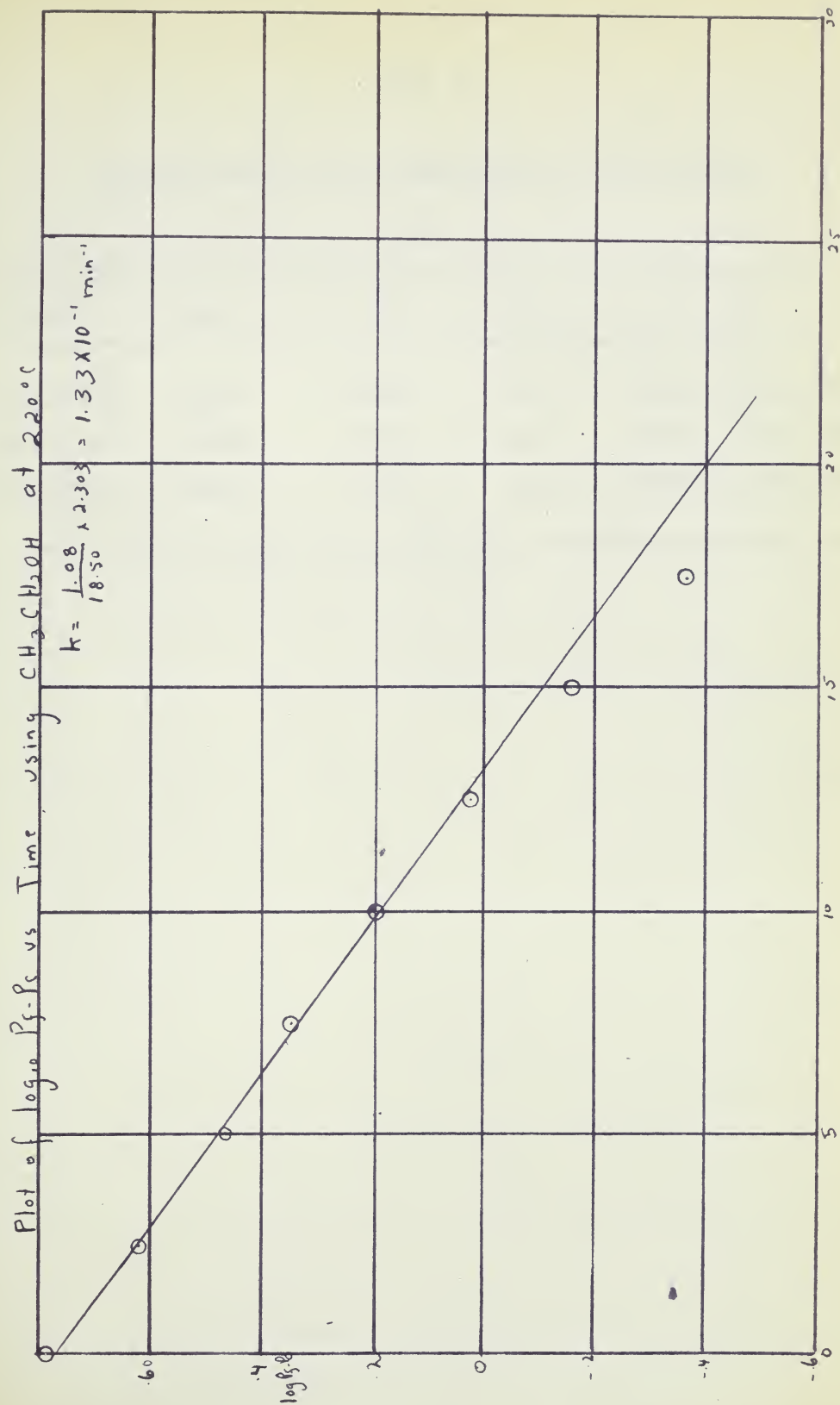
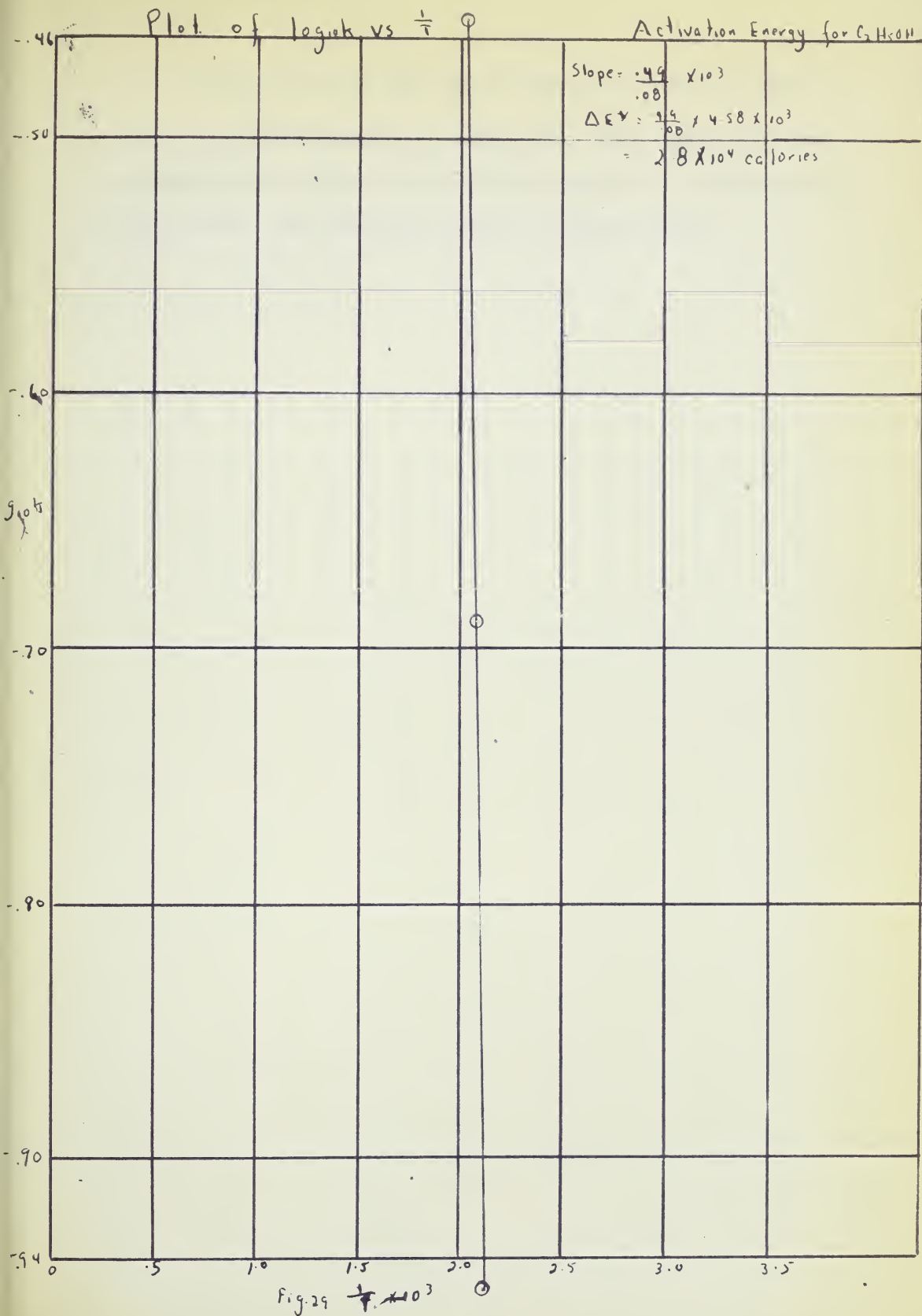


Fig. 28 Time - Minutes

TABLE XX

ACTIVATION ENERGY FOR THE DECOMPOSITION OF ETHYL ALCOHOL

$k \text{ min}^{-1}$	$\log k$	$t^{\circ}\text{C}$	$T^{\circ}\text{A}$	I/T
1.12×10^{-1}	-.9508	200	473	$.002114 = 2.11 \times 10^{-3}$
2.05×10^{-1}	-.6882	210	483	$.00207 = 2.07 \times 10^{-3}$
3.4×10^{-1}	-.4685	220	493	$.002028 = 2.028 \times 10^{-3}$



Figures 30 to 35 give similar results to methyl and ethyl alcohol for the decomposition of formic acid. Table XXVII gives the data necessary for finding the activation energy for the decomposition of formic acid. The activation energy is 15,300 calories.

DECOMPOSITION OF FORMIC ACID OVER CATALYST #8 AT 210°C

Temp. Line = 115°C

Temp. Furnace = 110°C

Temp. Reactor = 210°C

Pressure = 56.5 cms. Hg

TABLE XXI

Time		Press. cms. Hg	Press.
<u>Min.</u>	<u>Sec.</u>		
0	00	41.0	15.5
0	20	41.1	15.4
	30	41.0	15.4
2	02	40.0	16.5
3	15	39.0	17.5
4	46	38.0	18.5
5	58	37.0	19.5
7	37	36.0	20.5
9	00	35.0	21.5
10	40	34.0	22.5
12	05	33.0	23.5
14	28	32.0	24.5
16	45	31.0	25.5
19	30	30.0	26.5
22	06	29.0	27.5
26	06	28.0	28.5
30	11	27.0	29.5
36	00	26.0	30.5

TABLE XXII

$P_f = 23.10$					
Time - min.	Press. cms. Hg	Correction x	P - x	$P_f - P_c$	$\log P_f - P_c$
0					
2.5	16.9	.5	16.4	6.6	0.82
5.0	18.7	1.1	17.6	5.4	.73
7.5	20.5	1.6	18.9	4.1	.61
10.0	22.1	2.2	19.9	3.1	.49
12.5	23.5	2.7	20.8	2.2	.34
15.0	24.7	3.2	21.5	1.5	.18
17.5	25.8	3.8	22.0	1.0	0.00
20.0	26.8	4.3	22.5	.5	-.30
22.5	27.6	4.8	22.8	.8	-.70
25.0	28.3	5.3	23.0		
27.5	28.9	5.9	23.0		
30.0	29.4	6.4	23.0		

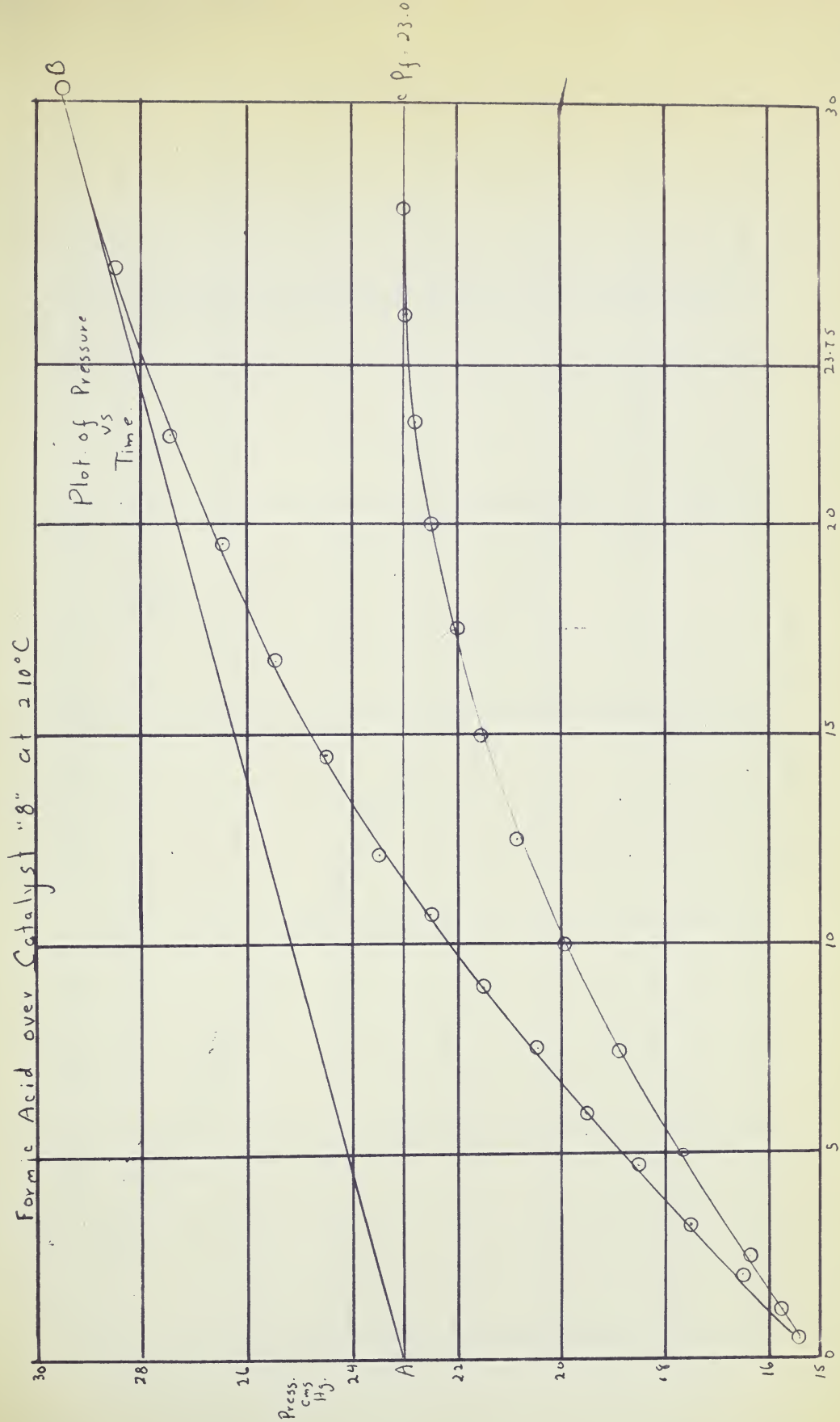


Fig. 30 Time-minute

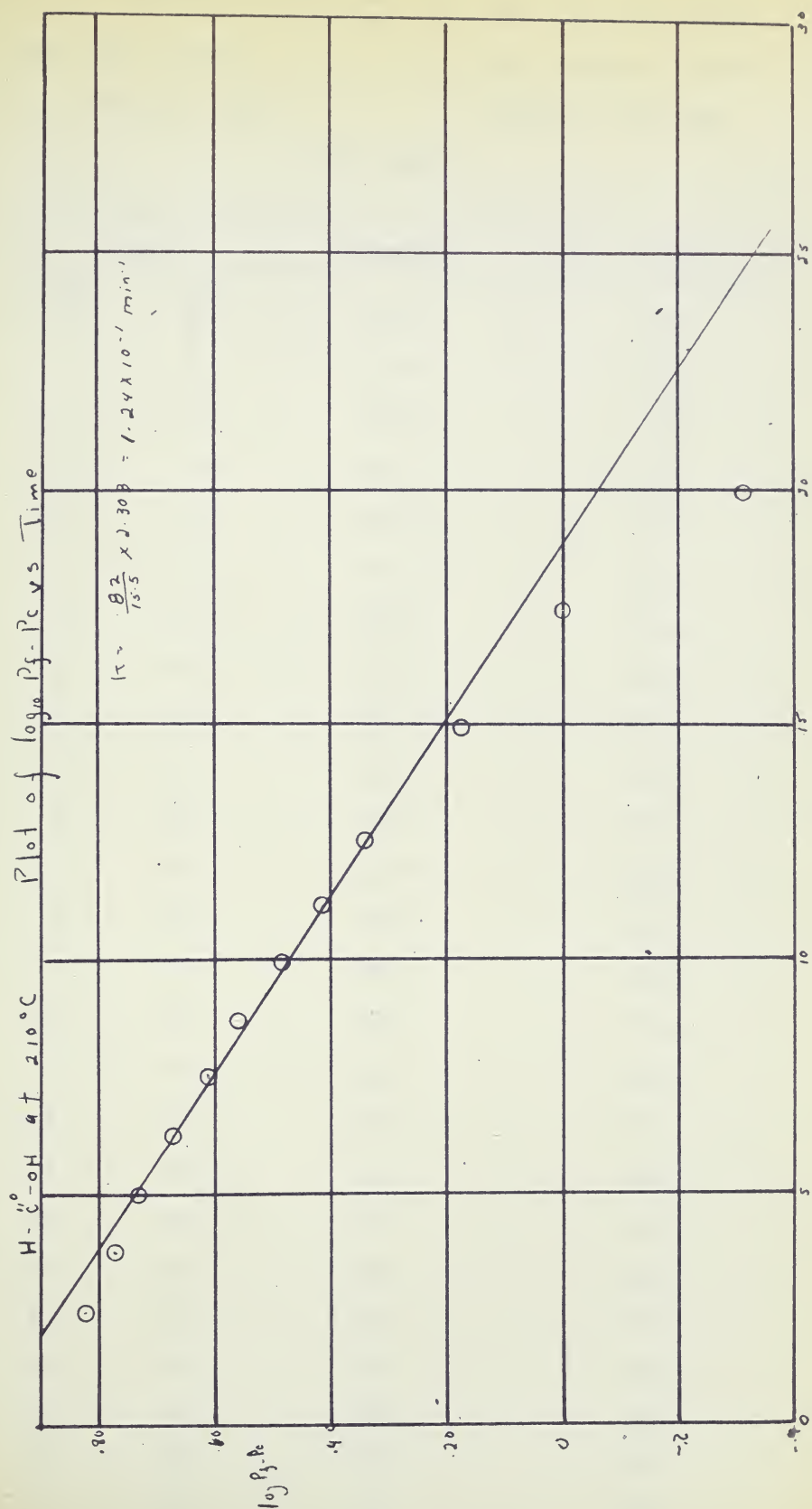


Fig. 31 Time - Minutes

DECOMPOSITION OF FORMIC ACID OVER CAT. #8 AT 220°C

Temp. Line = 120°C

Temp. Reactor = 220°C

Temp. Furnace = 116°C

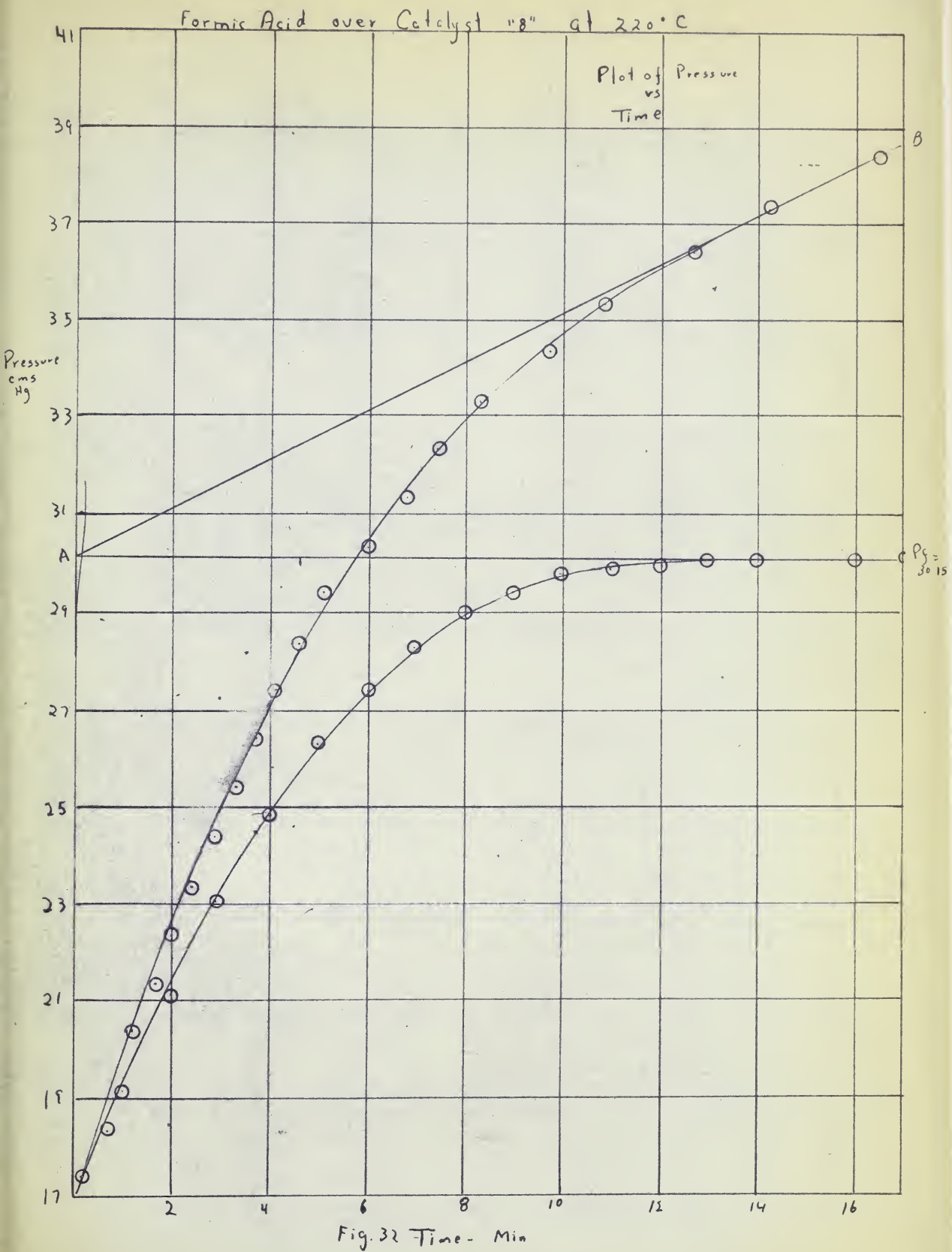
Pressure = 56.4 cms.

TABLE XXIII

Time		Press.	Press.
Min.	Sec.		
0	00	39.4	17.0
	11	39.0	17.4
	45	38.0	18.4
1	15	36.0	20.4
1	40	35.0	21.4
2	00	34.0	22.4
2	25	33.0	23.4
2	52	32.0	24.4
3	20	31.0	25.4
3	45	30.0	26.4
4	05	29.0	27.4
4	35	28.0	28.4
5	10	27.0	29.4
6	01	26.0	30.4
6	48	25.0	31.4
7	25	24.0	32.4
8	16	23.0	33.4
9	45	22.0	34.4
10	52	21.0	35.4
12	45	20.0	36.4
14	15	19.0	37.4
16	30	18.0	38.4
18	54	17.0	39.4
20	52	16.0	40.4
24	15	15.0	41.4

TABLE XXIV

$P_f = 30.15$			
Time	P_c	$P_f - P_c$	$\log P_f - P_c$
0	17.00	13.15	1.12
1	19.20	10.95	1.04
2	21.20	8.95	.95
3	23.00	7.15	.85
4	24.80	5.35	.73
5	26.20	3.95	.60
6	27.40	2.75	.44
7	28.30	1.85	.27
8	28.90	1.25	.10
9	29.50	.65	-.18
10	29.80	.35	-.46
11	29.90	.25	-.60
12	30.00	.15	-.82
13	30.10	.05	-1.30
14	30.15		
15	30.15		



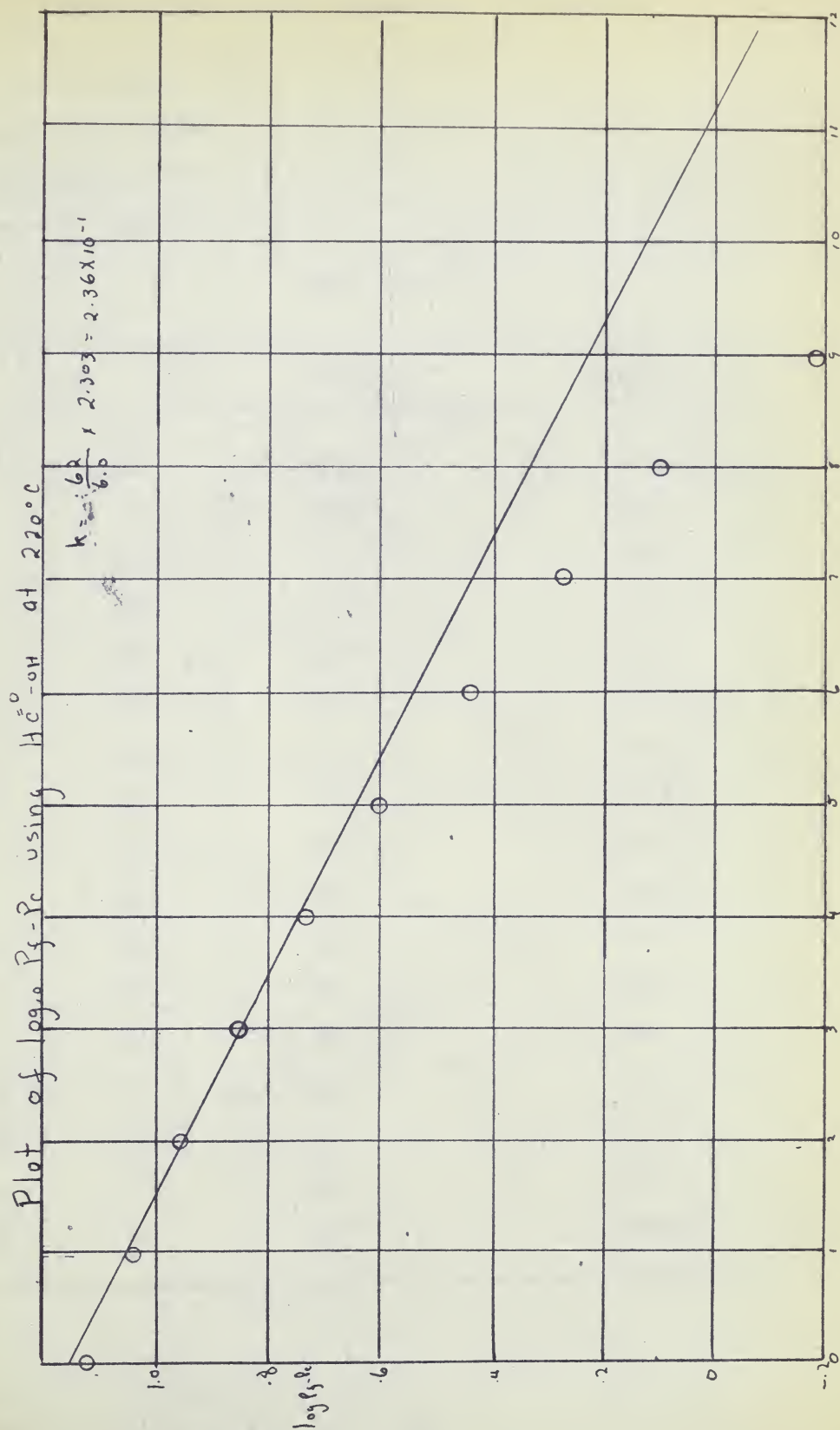


Fig.33 Time - Minutes

DECOMPOSITION OF FORMIC ACID OVER CAT. #8 AT 230°C

Temp. of Line = 115°C

Temp. of Furnace = 145°C

Temp. of Reactor = 230°C

Pressure = 56.0 cms. Hg

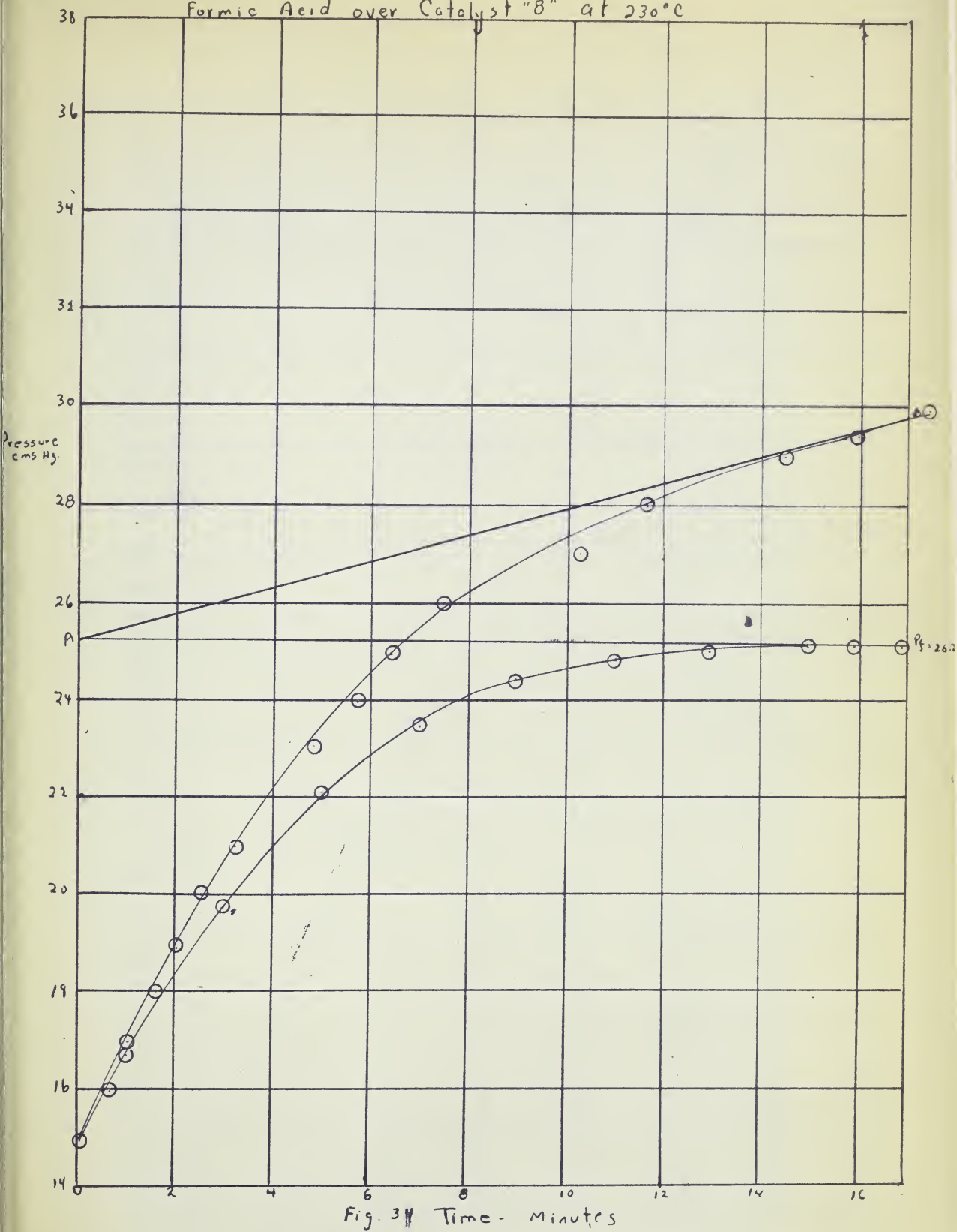
TABLE XXV

Time		Press.	Press. (56 - P)
Min.	Sec.		
0	00	41.2	14.8
	6	41.0	15.0
	40	40	16.0
1	07	39	17.0
1	37	38	18.0
2	01	37	19.0
2	34	36	20.0
3	20	35	21.0
4	00	34	22.0
4	52	33	23.0
5	39	32	24.0
6	25	31	25.0
7	30	30	26.0
10	18	29	27.0
11	38	28	28.0
14	30	27	29.0
17	35	26	30.0

TABLE XXVI

$P_f = 25.2$			
Time	P_c	$P_f - P_c$	$\log P_f - P_c$
0	14.8	10.4	1.02
1	16.6	8.6	.93
2	18.4	6.8	.84
3	19.8	5.4	.73
4	21.0	4.2	.62
5	22.0	3.2	.51
6	22.9	2.3	.36
7	23.5	1.7	.23
8	24.1	1.1	.04
9	24.5	.7	-.15
10	24.7	.5	-.30
11	24.9	.3	-.52
12	25.0	.2	-.70
13	25.1	.1	-1.00
14	25.2		
15			

Formic Acid over Catalyst "8" at 230°C



Plot of $\log_e P_f - P_e$ vs Time using $\text{HC}=\text{OH}$ at 230°C

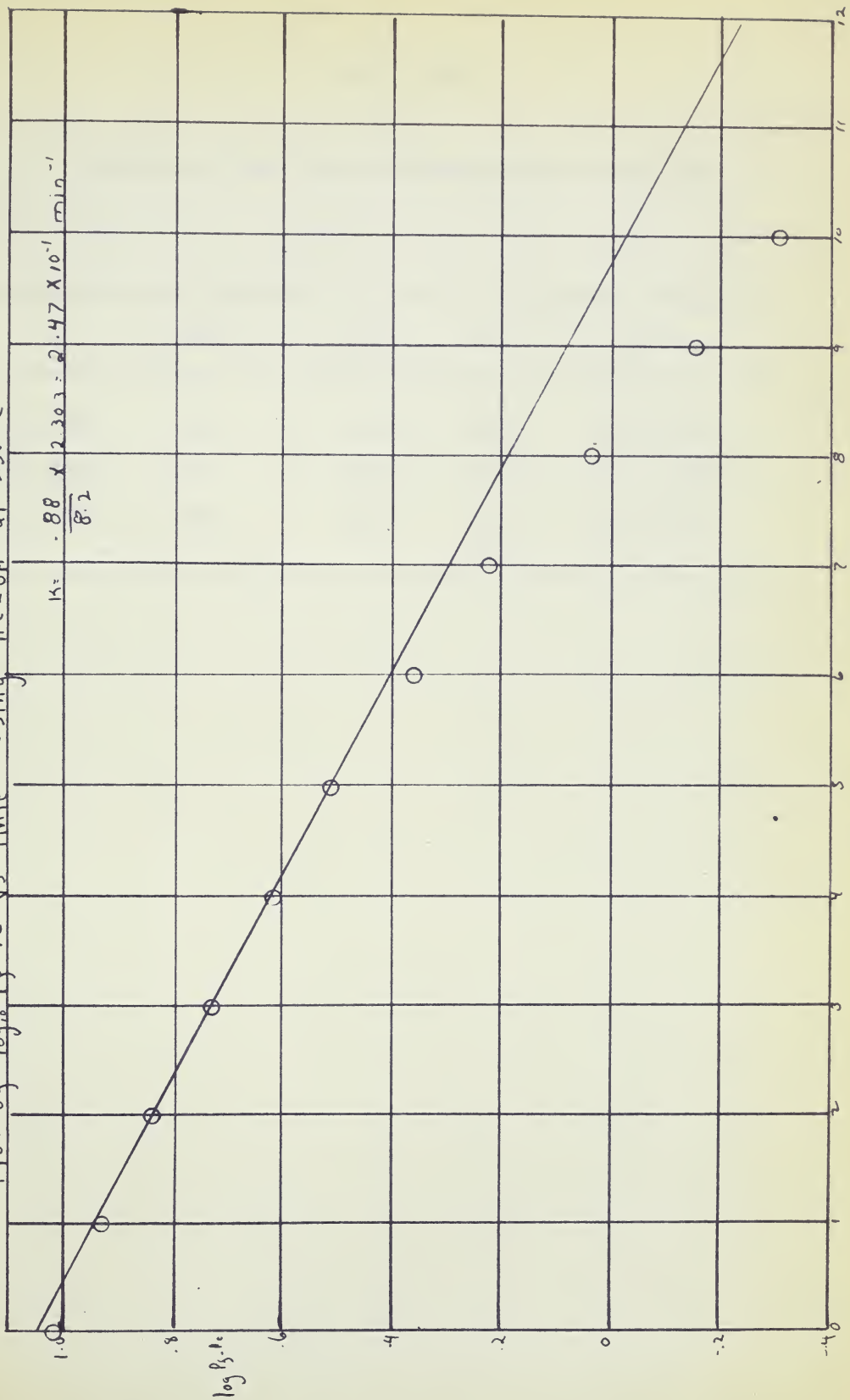
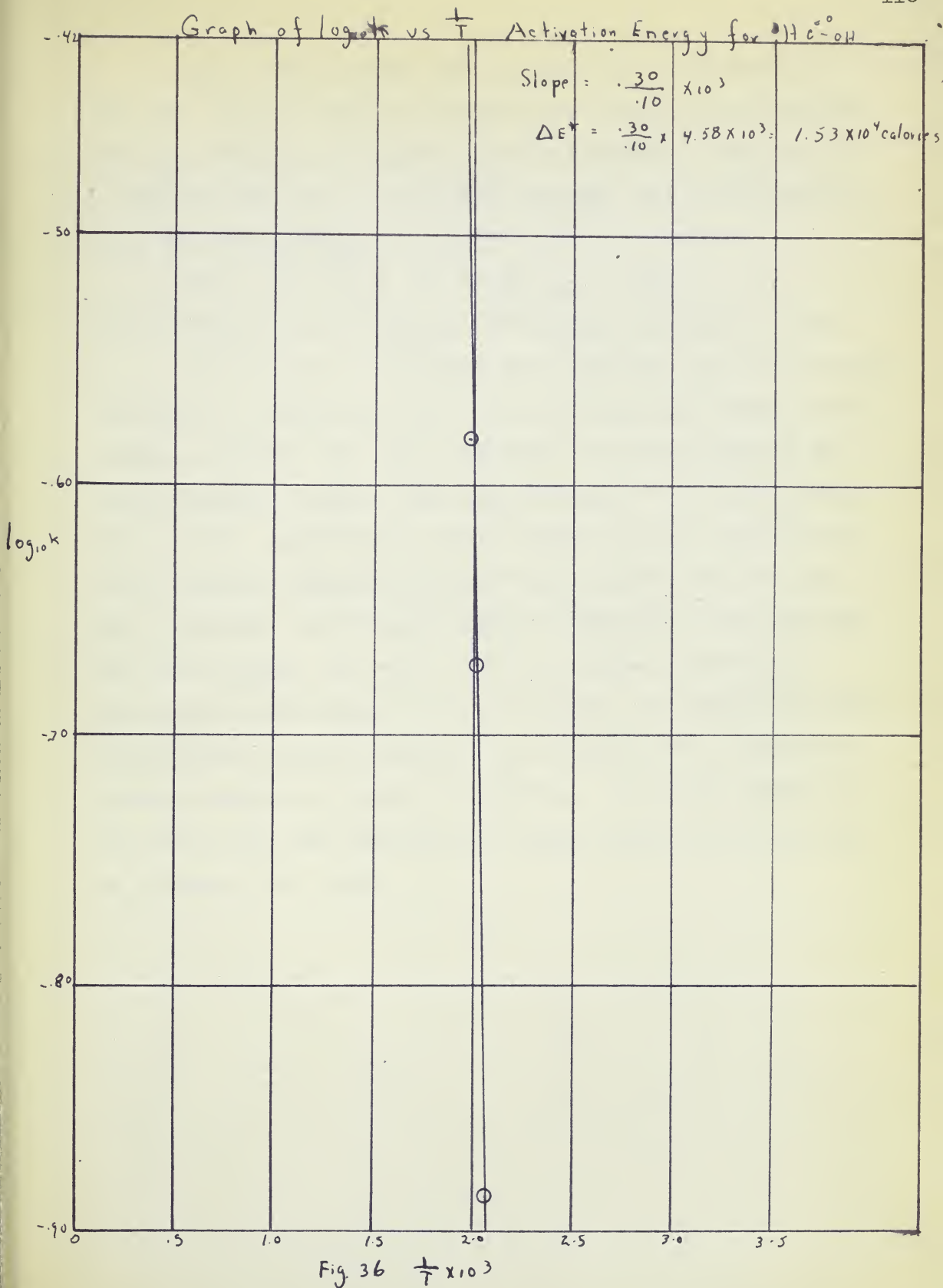


Fig. 35 Time - Minutes.

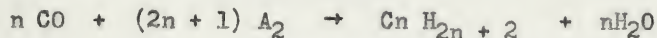
TABLE XXVII

ACTIVATION ENERGY FOR THE DECOMPOSITION OF FORMIC ACID

k	log k	t°C	T°A	1/T
1.30×10^{-1}	.886	210	483	2.07×10^{-3}
2.13×10^{-1}	.672	220	493	2.03×10^{-3}
2.62×10^{-1}	.582	230	503	1.99×10^{-3}



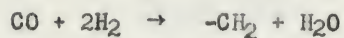
Tables XXVIII to XXXIII list the results for the synthesis of $2H_2 + CO$. In these tables it is shown that the pressure change decreases with time. Therefore the negative value for k obtained is indicative for a synthesis rather than a decomposition occurring. The reaction occurring is of the following type:



$\Delta l^\dagger = -267,600$ calories (exothermic) which gives a decrease in volume.

In these curves it is assumed that in the first part of the reaction one product is synthesized, then as the reaction proceeds another type of product is produced. The rate of formation of the first product by the reaction appears to follow a first order reaction as can be seen by Figs. 38, 40 and 42. Apparently the catalyst surface is nearly saturated with carbon monoxide. Hydrogen is then admitted and strikes the surface and will be adsorbed. As soon as the hydrogen is adsorbed it will react with the carbon monoxide. The rate at which the hydrogen is adsorbed is proportional to the hydrogen in the gaseous phase, thus indicating a first order reaction. Another explanation may be that the rate is independent of carbon monoxide and hydrogen concentration. The reaction depends on the rate at which some intermediate is formed, and that intermediate may be following a first order.

2 Parts H₂, 1 Part CO Over Catalyst #8 at 200°C



Temp. Line = 115°C

Temp. Reactor = 200°C

Temp. Furnace = 142°C

Pressure = 56.1 cms.

TABLE XXVIII

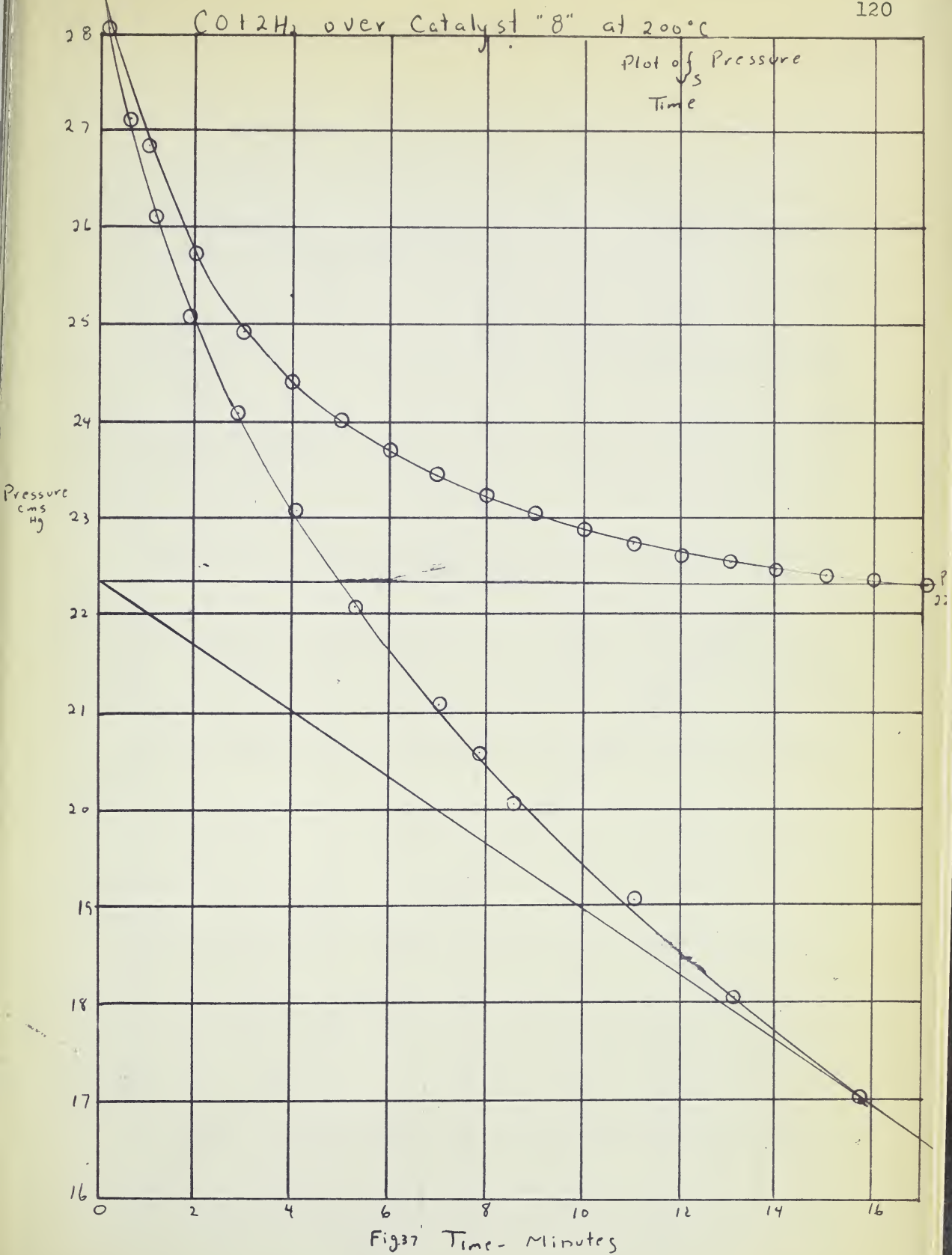
Min.	Time Sec.	Press. Cms. Hg	Press. Cms. Hg
0	00	27.0	29.1
	12	28.0	28.1
	38	29.0	27.1
1	10	30.0	26.1
1	56	31.0	25.1
2	51	32.0	24.1
4	10	33.0	23.1
5	20	34.0	22.1
7	05	35.0	21.1
7	50	35.5	20.6
8	36	36.0	20.1
11	05	37.0	19.1
13	10	38.0	18.1
15	45	39.0	17.1
18	55	40.0	16.1
24	10	41.0	15.1

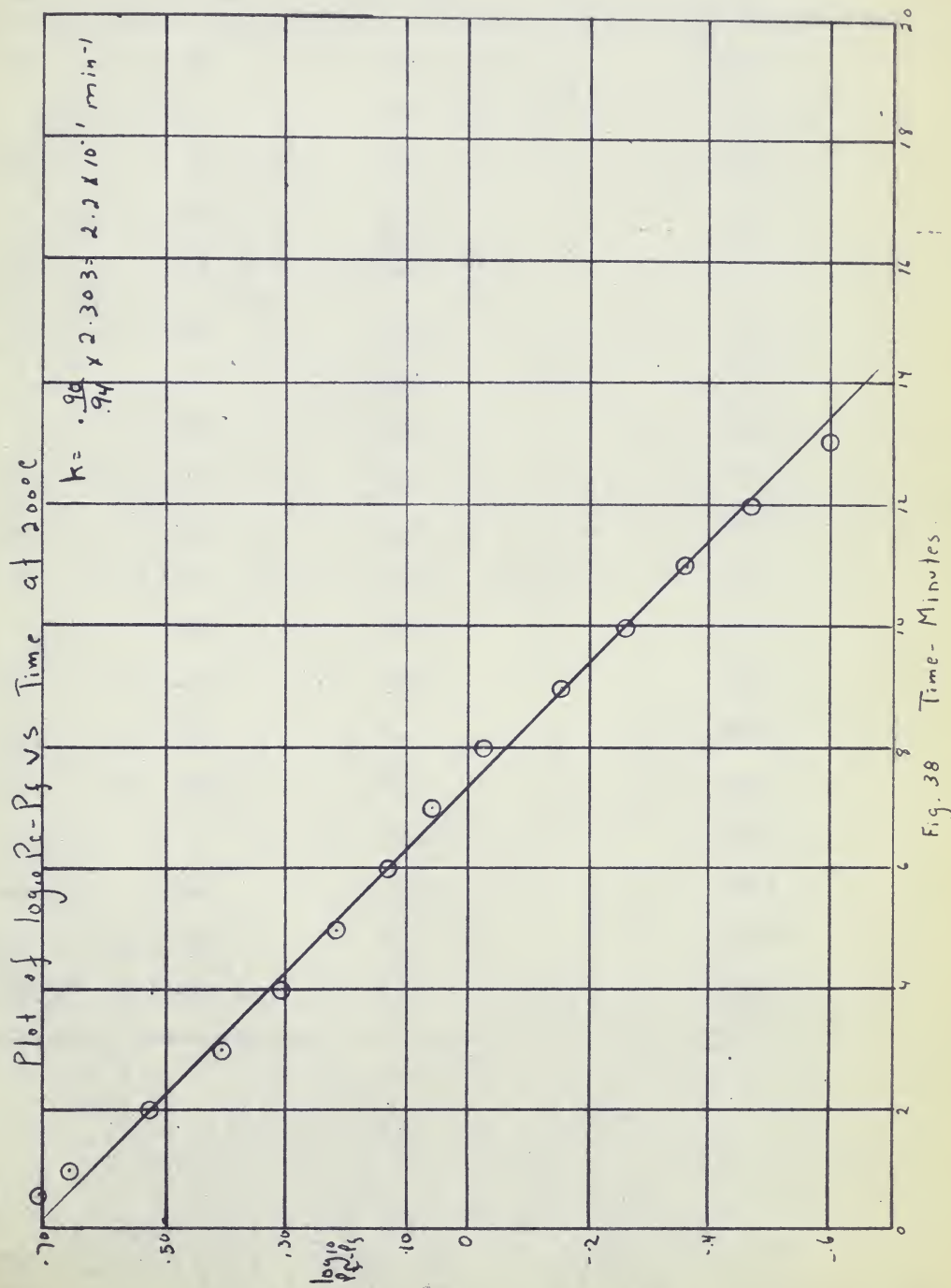
TABLE XXIX

CO + 2H₂ at 200°C

$$P_f = 22.35$$

Time Min.	P _c	P _c - P _f	log P _c - P _f
.6	27.5	3.15	.71
1	26.9	4.55	.66
2	25.9	3.35	.53
3	24.9	2.55	.41
4	24.4	2.05	.31
5	24.0	1.65	.22
6	23.7	1.35	.13
7	23.3	1.15	.06
8	23.25	.95	-.02
9	23.05	.70	-.15
10	22.9	.55	-.26
11	22.8	.45	-.35
12	22.65	.35	-.46
13	22.55	.20	-.70
14	22.50	.15	-.82
15	22.43	.08	-1.10
16	22.40	.05	-1.30
17	22.35		





Temp. Line = 115°C

Temp. Reactor = 210°C

Temp. Furnace = 142°C

Pressure = 56.0 cms.

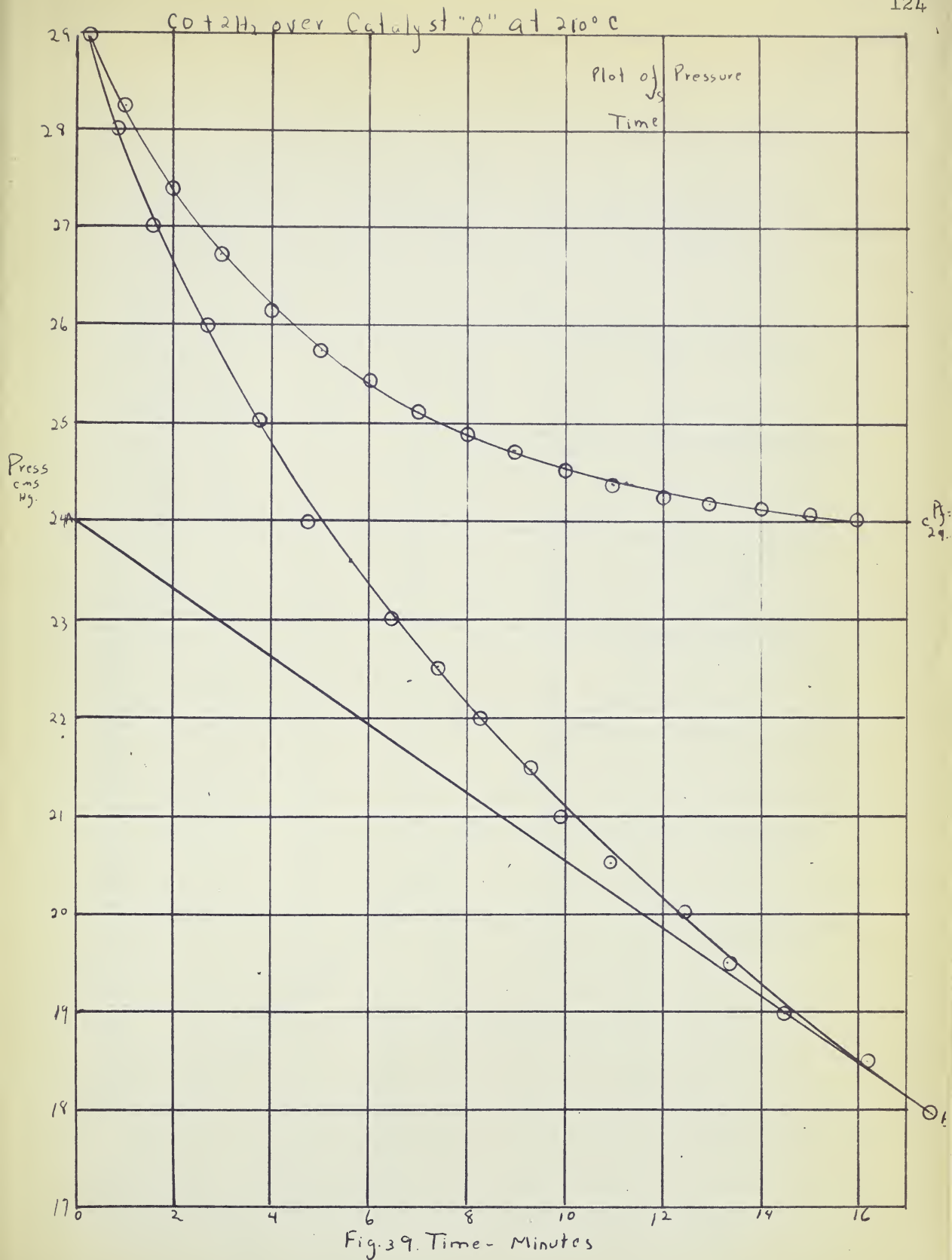
TABLE XXX

Min.	Time Sec.	Press. cms. Hg	Press.(56.0 - P)
0	00	26.5	29.5
	15	27.0	29.0
	51	28.0	28.0
1	31	29.0	27.0
2	40	30.0	26.0
3	45	31.0	25.0
4	45	32.0	24.0
6	25	33.0	23.0
7	24	33.5	22.5
8	15	34.0	22.0
9	13	34.5	21.5
9	58	35.0	21.0
10	55	35.5	20.5
12	26	36.0	20.0
13	20	36.5	19.5
14	31	37.0	19.0
16	12	37.5	18.5
17	30	38.0	18.0
24	46	40.0	16.0

TABLE XXXI

$$P_f = 24.0$$

Time	P_c	$P_c - P_f$	$\log P_c - P_f$
.3	29.0	5.0	.70
.1	28.2	4.2	.62
2	27.85	3.85	.59
3	26.7	2.7	.43
4	26.2	2.2	.34
5	25.75	1.75	.24
6	25.4	1.40	.15
7	25.15	1.15	.06
8	24.90	.90	-.05
9	24.70	.70	-.15
10	24.50	.50	-.30
11	24.40	.40	-.40
12	24.30	.30	-.52
13	24.20	.20	-.70
14	24.15	.15	-.82
15	24.09	.09	-1.05
16	24.05	.05	-1.30
17	24.00		



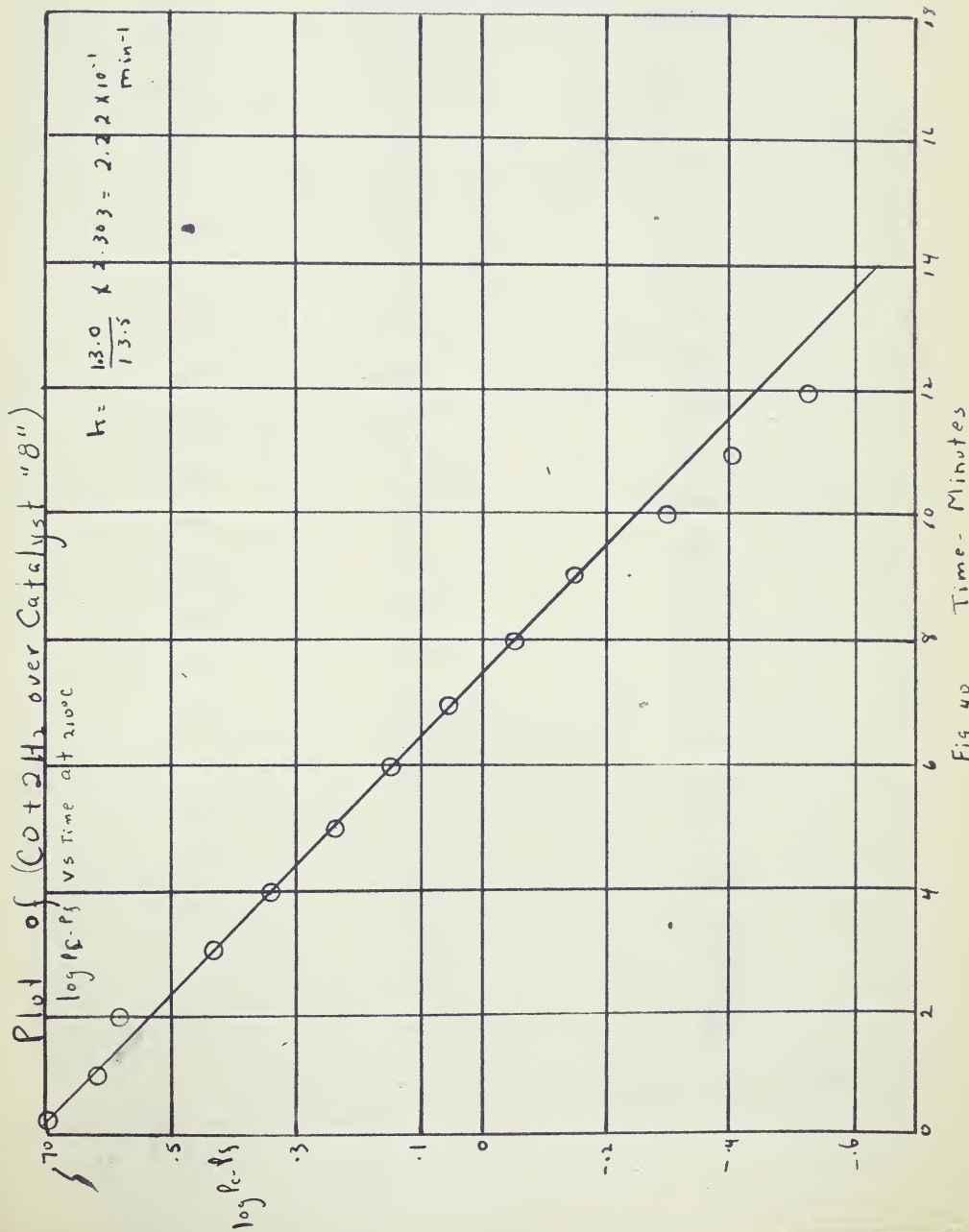


Fig. 40

CO + 2H₂ at 220°C over Catalyst "C"

Temp. Line = 120°C

Temp. Reactor = 220°C

Temp. Furnace = 142°C

Pressure = 56.0 cms. Hg

TABLE XXXII

Min.	Time Sec.	Press. cms. Hg	Press cms. Hg
0	00	21.5	35.4
	18	22.0	34.9
	41	22.5	34.4
	58	23.0	33.9
1	35	24.0	32.9
2	00	24.5	32.4
2	35	25.0	31.9
3	05	25.5	31.4
3	36	26.0	30.9
3	58	26.5	30.4
4	28	27.0	29.9
5	02	27.5	29.4
6	07	28.0	28.9
6	55	28.5	28.4
7	29	29.0	27.9
8	02	29.5	27.4
8	46	30.0	26.9
10	22	30.5	26.4
11	28	31.0	25.9
12	03	31.5	25.4
12	55	32.0	24.9
15	05	32.5	24.4
15	57	33.0	23.9
18	05	33.5	23.4

TABLE XXXIII

CO + 2H₂ at 220°CP_f = 28.2

Time	P _c	P _c - P _f	log P _c - P _f
.3	35.0	6.3	.80
1	34.1	5.4	.73
2	33.2	4.5	.65
3	32.5	3.8	.58
4	31.8	3.1	.49
5	31.15	2.45	.39
6	30.60	1.90	.28
7	30.10	1.40	.15
8	29.80	1.10	.04
9	29.50	.80	-.10
10	29.30	.50	-.30
11	29.15	.45	-.35
12	29.0	.3	-.52
13	28.9	.2	-.70
14	28.85	.15	-.82
15	28.80	.10	-1.0
16	28.75	.05	-1.30
17	28.7		

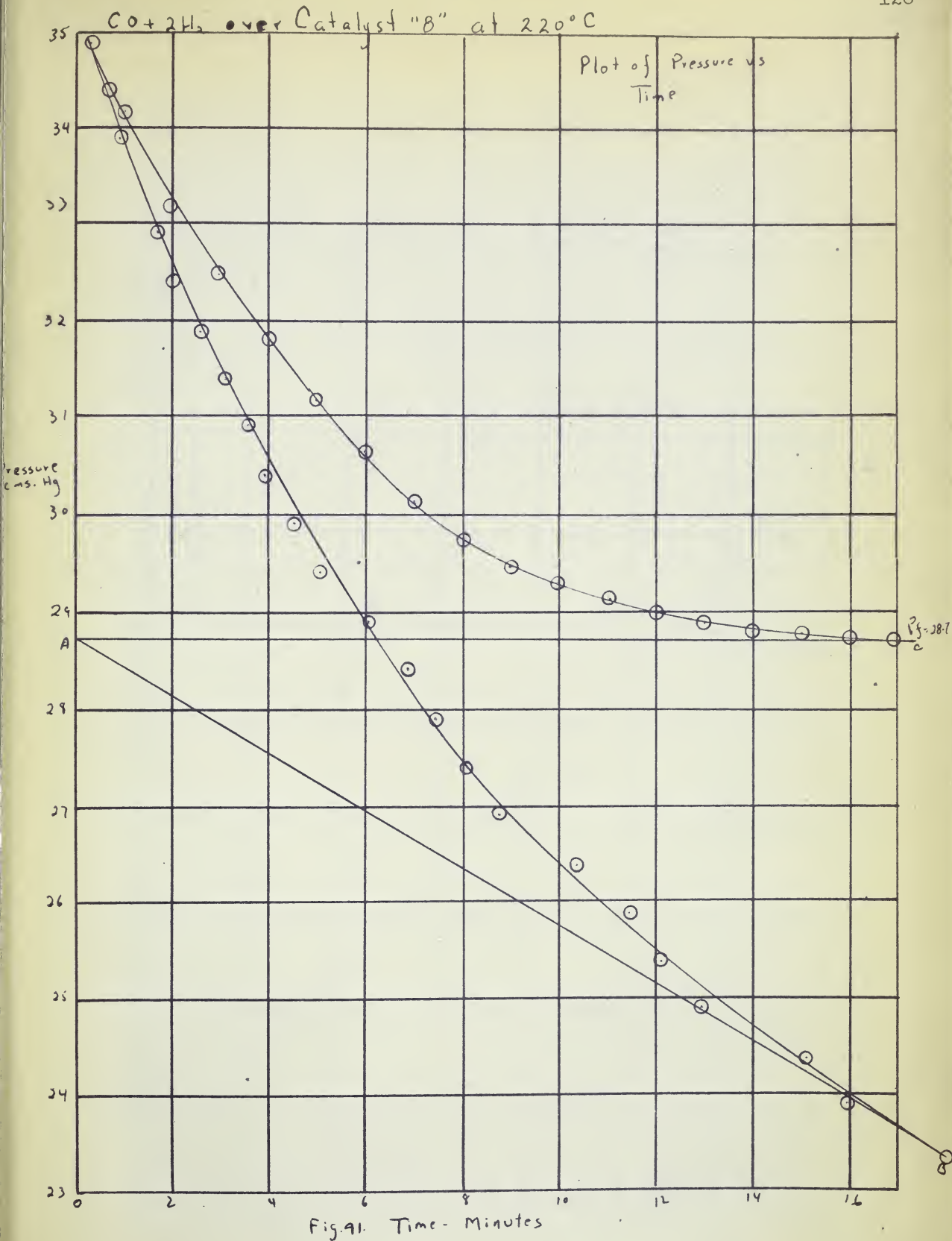


Fig. 91. Time - Minutes

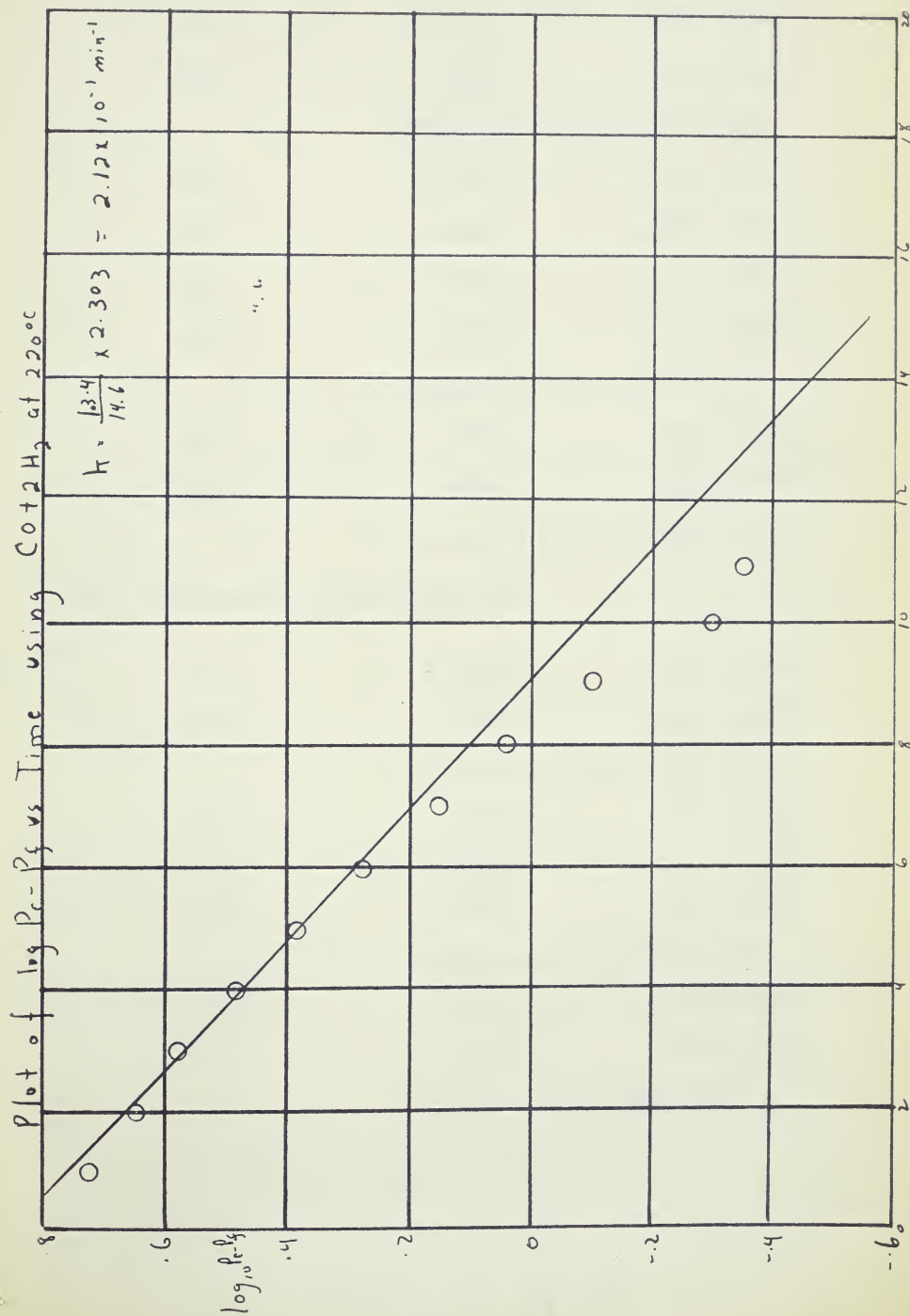


Fig 92. Time - Minutes

TABLE XXXIV

Comparisons of Rates of Decomposition of MeOH, ETOH and Formic Acid

MeOH (Absolute)

Run No.	Temp. °C	k min ⁻¹
17M	190°C	1.17 x 10 ⁻¹
18M	190°C	1.06 x 10 ⁻¹
Average k = 1.11 x 10 ⁻¹ min ⁻¹		
19M	210°C	1.50 x 10 ⁻¹
20M	210°C	2.02 x 10 ⁻¹
21M	210°C	2.7 x 10 ⁻¹
22M	210°C	2.9 x 10 ⁻¹
Average k = 2.8 x 10 ⁻¹ min ⁻¹		
23M	200°C	1.96 x 10 ⁻¹
24M	200°C	1.98 x 10 ⁻¹
Average k = 1.97 x 10 ⁻¹		

$$\Delta E^* \text{ (Graphical)} = 2.23 \times 10^4 \text{ cal.}$$

ETOH (98%)

28E	200°C	1.08 x 10 ⁻¹
29E	200°C	1.16 x 10 ⁻¹
Average k = 1.12 x 10 ⁻¹ min ⁻¹		
30E	210°C	1.9 x 10 ⁻¹
31E	210°C	2.2 x 10 ⁻¹
32E	210°C	2.04 x 10 ⁻¹
Average = 2.05 x 10 ⁻¹ min ⁻¹		
33E	220°C	3.30 x 10 ⁻¹
34E	220°C	3.52 x 10 ⁻¹
Average = 3.4 x 10 ⁻¹ min ⁻¹		

$$\Delta E^* \text{ (Graphical)} = 2.8 \times 10^4 \text{ cal.}$$

Formic Acid

Run No.	Temp. °C	k min ⁻¹
38 _F	210°C	1.24 x 10 ⁻¹
39 _F	210°C	1.5 x 10 ⁻¹
40 _F	210°C	1.15 x 10 ⁻¹ min ⁻¹
Average = 1.30 x 10 ⁻¹ min ⁻¹		
41 _F	220°C	2.36 x 10 ⁻¹
42 _F	220°C	1.90 x 10 ⁻¹
Average = 2.13 x 10 ⁻¹ min ⁻¹		
43 _F	230°C	2.77 x 10 ⁻¹
44 _F	230°C	2.47 x 10 ⁻¹
Average = 2.62 x 10 ⁻¹		

$$\Delta E^* = 1.53 \times 10^4 \text{ cal.}$$

COMPARISON OF RATES FOR CO + 2H₂ AT DIFFERENT TEMPERATURES

<u>Temperature</u>	<u>Run</u>	<u>k. min⁻¹</u>
200°C	45 _c	2.2 x 10 ⁻¹
	46 _c	2.1 x 10 ⁻¹
	Average = 2.1 x 10 ⁻¹	
210°C	49	2.2 x 10 ⁻¹
	50	1.90 x 10 ⁻¹
	Average = 2.1 x 10 ⁻¹	
220°	51	2.12 x 10 ⁻¹
	52	2.02 x 10 ⁻¹
	Average = 2.07 x 10 ⁻¹ 2.1 x 10 ⁻¹	

CONCLUSION

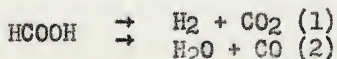
The results of the decomposition of CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ and HCOOH and the synthesis of $\text{CO} + 2\text{H}_2$ are listed in Table XXXIV.

From the data of Table XXXIV it can be seen that at temperatures commonly encountered in the synthesis of hydrocarbons below 200°C the decompositions are lower than synthesis rate for hydrocarbons.

If this first order reaction rate for $\text{CO} + 2\text{H}_2$ is faster than that for methanol, ethanol and formic acid, it indicates that the latter cannot be an intermediate step in the Fischer Tropsch synthesis at temperatures below 200°C . However, above 200°C the evidence does not remove the possibility that they are intermediate steps in the synthesis.

The activation energies for methanol, ethanol, and formic acid over a $\text{Co} : \text{ThO}_2 : \text{Mg} : \text{Kieselguhr}$ catalyst were found to be 22,300 calories, 28,000 calories, and 15,300 calories respectively.

Formic acid decomposes in the two ways:



On the surface of glass, in the neighborhood of 280°C the alternative reactions take place with nearly equal speeds, yet the heats of activation are very different. E_{co} , the heat of activation associated with the decomposition into carbon monoxide and water, is about 16,000 calories, while E_{co_2} is about 28,000 calories. From this data it appears that the reaction taking place over the $\text{Co} : \text{Thoria} : \text{MgO}$ catalyst is (2) i.e. the formation of $\text{H}_2\text{O} + \text{CO}$. The table below E_{co_2} represents the apparent heat of activation in the decomposition of formic acid vapor into carbon dioxide and hydrogen.

<u>Surface</u>	<u>E_{co_2}</u>
Glass	24,500
Gold	23,500
Silver	31,000
Platinum	22,000
Rhodium	25,000.

Croxford and Rideal reported the decomposition of ethanol at the surface of a thorium catalyst to have an activation energy of 30,000 calories. The value for the activation energy obtained compares favorably for the decomposition of ethyl alcohol in this investigation.

From the International Critical Tables^{13A} the energy of activation for gaseous methanol was found to be 21,300 calories, which compares favorably with the results obtained.

Eidus^{8A} has also investigated the hypothesis that methanol, ethanol and formic acid were intermediate in the synthesis of hydrocarbons. In his investigation, he determined reaction products formed when these compounds were passed over a Co : ThO₂ : MgO : kieselguhr catalyst and did not investigate the rates of the reaction. From his work he concluded that methanol, ethanol and formic acid are not intermediate in the synthesis of hydrocarbons. The work reported here supports Eidus' conclusions.

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